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AND

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PUBLICATIONS OF THE SOCIETY.

With the exception of certain numbers of the Journals and Proceedings which are out of print, the following publications may be obtained from Messrs. Gurney and Jackson, 33, Paternoster Row, E.C.4.

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		£	s.	d.	£	s.	d.
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‡ Post free to Fellows.

The Journal, which is published on the last day of each month includes the Proceedings and Transactions of the Chemical Society and Abstracts of chemical papers.

The Annual Reports on the Progress of Chemistry contain an epitome of the principal definite steps in advance which have been made during the year. Fellows can obtain from the Assistant Secretary cases for binding the Annual Reports, price One Shilling each.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 6th, 1918, at 8 p.m., Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

It was announced that the Society has lost, through death, the following Fellows:

	<i>Elected.</i>	<i>Died.</i>
Waller Augustus Handcock	Dec. 6th, 1900	May 26th
Henry Tylston Hodgson	Apr. 17th, 1873	May 22nd
Mulgrave Daniel Penney	Mar 7th, 1870	Mar. 5th

Messrs. A. Geake, K. G. Laiwala, and R. Brightman were formally admitted as Fellows of the Chemical Society.

Certificates for election were read for the first time in favour of:

Frank Bainbridge, Woodland View, West Road, Loftus-in-Cleveland.
 Reginald Percy Leopold Britton, 58, The Crescent, Wimbledon Park, S.W.19.
 John Edwyn Davies, B.Sc., Taimawr, Swansea Road, Merthyr Tydvil.
 Campbell Falconer, the Hall, Osbaldwick, York.
 Bernard Arthur James Jeffs, 35b, Gladstone Avenue, Wood Green, N.22.
 Edwin Percy Keeble, Summer Lodge, Kenilworth.
 Albert Victor Mountford, 38, Gamblins Road, St. Martins, Christchurch, New Zealand.
 Frederick Gerald Tryhorn, M.Sc., 45, Hallville Road, Mossley Hill, Liverpool.
 Gerald Noel White, B.Sc., 15, West End Avenue, Pinner, Middlesex.
 John William Reginald Youll, "Keswick," Rainsford Avenue, Chelmsford..

Dr. Horace T. Brown then delivered his lecture, entitled "The Principles of Diffusion; their Analogies and Applications." A vote of thanks to Dr. Horace T. Brown for his lecture, proposed by Professor P. F. Frankland and seconded by Professor Farmer, was carried with acclamation.

Ordinary Scientific Meeting, Thursday, June 20th, 1918, at 8 p.m., Mr. A. CHASTON CHAPMAN in the Chair.

It was stated that the following Fellows had died:

	Elected.	Died.
Thomas Farries	Dec. 1st, 1870.	June 5th.
Alexander Milne	May 7th, 1885.	May 29th.

The following announcements were made:

(1) That a communication had been received from the Committee of the Van't Hoff Fund for the endowment of research in pure and applied chemistry. The amount from this fund available for distribution during 1919 is about £150.

A Committee, consisting of Professor A. F. Holleman (President), Professor S. Hoogewerff, Professor A. Smits, and Professor E. H. Büchner (Secretary), has been appointed to award grants. Applications should be sent before November 1st, 1918, by registered post, to "Het Bestuur der Koninklijke Akademie van Wetenschappen; bestemd voor de Commissie van het 'Van't Hoff-fonds' Trippenhuys, Kloveniersburgwal, te Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.

(2) The Council have decided to issue the List of Fellows in the near future; it will not be circulated in the usual manner, but may be procured by Fellows on applying to the Assistant Secretary.

(3) In view of the shortage of paper, the Council wish to emphasise the necessity of authors reducing as far as possible the length of scientific communications submitted to the Society.

(4) The Council have appointed a Committee, consisting of the following, Messrs. W. R. Bousfield, A. G. Green, C. A. Hill, G. T. Morgan, A. Scott, and W. P. Wynne, and the Officers, namely, Messrs. W. J. Pope, M. O. Forster, S. Smiles, J. C. Philip, and A. W. Crossley, to consider the revision of the Bye-laws. Opportunity will be afforded to Fellows for bringing forward suggestions on the matter.

Certificates of candidates for election were read for the first time in favour of:

Claud Diamond, B.Sc., 17, Moresby Road, Upper Clapton, E.5.
John Edward Doodson, Smithy Bridge, Rochdale.

John Robert Douglas, A.R.C.S.I., West-field, Saltcoats, B.O., Ayrshire.
 Laurence Francis Le Brocq, B.Sc., "Akender," Guildford Road, South
 Farnborough, Hants.
 Donald Neil McArthur, B.Sc., 28, Grafton Street, Glasgow.
 George Frederick Robertshaw, Mornay, Kearsley Road, Higher Crumpsall,
 Manchester.
 Eric Sinkinson, 14A, Albert Bridge Road, S.W.11.
 Thomas Rinck Stopford, M.Sc., "Woodbank," Macclesfield.

Certificates for election have been authorised by the Council for
 presentation to ballot under Bye-Law I(3) in favour of:

James Garfield Anderson, M.Sc., Southland Boys' High School, Invercargill,
 New Zealand.
 Juan Pedigo Charles Chandrasena, B.Sc., Technical Schools, Colombo, Ceylon.

Messrs. F. H. Lowe and J. Reilly were elected Scrutators, and
 a ballot for the election of Fellows was held. The following were
 subsequently declared duly elected as Fellows.

William Baird.	Fred Henesey, B.Sc.
George Henry Rowland Barham.	John Bright Hoblyn.
Joseph Gault Bearn, M.Sc.	John Laurence Pitchford Holling-
Joseph William Bell.	worth.
George Rowland Bolsover.	James Henry Lindfield.
Henry Aldous Bromley.	Ben Lockspeiser, M.A.
Albert Eric Cashmore.	Francis John McConnell.
Roland Lebeg Townley Clarkson.	Alfred Zygmunt Molteni.
John William Cobb.	Edgar Newbery, D.Sc.
Hubert William Dailey.	Edward Churton Powell.
Thomas William Derrington.	Madyar Gopal Rau, M.A.
George William Dunster.	Bertram Leonard Read, B.Sc.
Arthur Broughton Edge.	Runar Ivar Olsson Seffer.
Stanley Elliott, B.Sc.	Alan Speedy.
Robert Ellison.	Louis Stott.
Francis William Fitzgerald.	John Thomas, B.A., D.Sc.
Sidney Fleminger.	John Turnbull.
Frank Scott Fowweather, M.Sc.	Richard Henry Vernon, Ph.D.
Stanley Joseph Green, B.A.	Hubert Charles Siegfried de Whalley.
Nalini Mohan Gupta, M.Sc.	William Whyte.
Ernst Johannes Hartung, M.Sc.	Samuel Walter Woolley.

The following papers were read:

"The equilibrium isotherm of association in organic solutions the
 solvent of which is unassociated as pure liquid." By W. R.
 INNES.

"Diazoimides of nitro- and 2:6-dichloro-*p*-phenylenediamine."
 By G. T. MORGAN and D. A. CLEAGE.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

DUBOSC, A., and LUTTRINGER, A. Rubber: its production, chemistry and synthesis in the light of recent research. A practical handbook for the use of rubber cultivators, chemists, economists and others. English edition by EDWARD W. LEWIS. London 1918. pp. xi+383. ill. 21s. net. (*Recd.* 6/6/18.)

From the Publishers: Messrs. Charles Griffin.

PLIMMER, ROBERT HENRY ADERS. Practical organic and bio-chemistry. New and revised edition. London 1918. pp. xii+636. ill. 18s. net. (*Recd.* 3/6/18.)

From the Publishers: Messrs. Longmans, Green and Co.

RAMSAY, SIR WILLIAM. See TILDEN, SIR WILLIAM A.

TILDEN, SIR WILLIAM A. Sir William Ramsay, K.C.B., F.R.S. Memorials of his life and work. London 1918. pp. xvi+311. ill. 10s. net. (*Recd.* 6/6/18.)

From the Author.

YOUNG, SYDNEY. Stoichiometry. 2nd edition. London 1918. pp. xiv+363. ill. 12s. 6d. net. (*Recd.* 4/6/18.)

From the Publishers: Messrs. Longmans, Green and Co.

II. *By Purchase.*

BROWNING, CARL HAMILTON. Applied bacteriology. Studies and reviews of some present-day problems. London 1918. pp. xiii+291. ill. 7s. 6d. net. (*Recd.* 12/6/18.)

CHEMICAL MANUFACTURERS' DIRECTORY of England, Wales and Scotland, with some of the firms in Ireland, for 1918. Being a list of the principal manufacturers of chemicals used in commerce, medicine, agriculture, and the arts. 50th edition. London 1918. pp. 235. 3s. 6d. net. (*Reference.*)

COLLINS, SYDNEY HOARE. Plant products and chemical fertilizers. London 1918. pp. xvi+236. 7s. 6d. net. (*Recd.* 12/6/18.)

PRESIDENTIAL ADDRESS.

Reprints of the President's Address delivered before the Chemical Society on March 21st will be ready in July. Those Fellows desirous of assisting the Council in the circulation of this Address are reminded that copies can be obtained from the Assistant Secretary free of charge.

properties of *cyclodihydromyrcene* (*Ber.*, 1901, **34**, 3128) and of *cyclolinaloolene* (*Ber.*, 1894, **27**, 2521):

	Hydrocarbon from spinacene.	<i>cyclo</i> Dihydro- myrcene.	<i>cyclo</i> Linaloolene.
Molecular formula	$C_{10}H_{18}$	$C_{10}H_{18}$	$C_{10}H_{18}$
Boiling point	170–176°	169–172°	165–167°
Specific gravity	0.815	0.828	0.811
Refractive index	1.459	1.462	1.460
Number of atoms of bromine added	Two	Two	Two

Had time permitted, specimens of *cyclodihydromyrcene* and of *cyclolinaloolene* would have been prepared for the purpose of making a fuller comparison. This I hope will be done at some future time. In the above work, steps were taken to make it quite clear that this terpenic hydrocarbon was not formed by the action of sodium on the small amount of oxygenated constituent occurring in the spinacene used. To this end, the spinacene, after having been distilled over a considerable excess of sodium under 10 mm. pressure, was then redistilled over a further quantity of sodium under 40 mm. pressure. From the distillate, the terpenic hydrocarbon described above was separated by steam distillation. The recovered and unchanged spinacene was then for a third time distilled over sodium under 40 mm. pressure, with the result that a further quantity of the terpenic hydrocarbon was obtained. There can, therefore be no reasonable doubt that this *cyclodihydromyrcene* does, in fact, result from the breaking up of the spinacene molecule. The view which I ventured to put forward in my first communication, that spinacene would prove to be related in some way to the terpenes, is therefore correct. The presence in large quantities in fish-liver oil of a complex hydrocarbon closely related to the terpenes is, I think, of very considerable interest both from the chemical and from the physiological points of view. In this connexion, it may be recalled that there is very strong evidence that cholesterol, a substance having nearly the same number of carbon atoms in its molecule as spinacene and occurring also in fish-liver oils, is a complex terpene compound.

The second fraction obtained from the decomposition of spinacene was also a fragrant, tolerably mobile liquid, boiling at 109–115°/10 mm., having an average molecular weight of about 190 and a specific gravity at 15°/15°=0.868 and at 20°/20°=0.865. This, as well as the viscous products left in the distillation flask, which doubtless consist of polymerisation products formed during the process, will, it is hoped, be subjected later on to a further study. Except perhaps in one direction in which results of industrial

importance may be anticipated, the further examination of spinacene and its derivatives will have to remain in abeyance until more normal conditions again prevail.

I desire to express my thanks to Miss D. J. Minter and Mr. C. W. McHugo for valuable assistance in connexion with this work.

8 DUKE STREET,
ALDGATE, E.C.3.

[Received, May 2nd, 1918.]

XL.—*Metallic Derivatives of Alkaloids.*

By JITENDRA NATH RAKSHIT.

HAVING prepared the metallic derivatives of acid amides (T, 1913, 103, 1557) it was thought that the metallic derivatives of alkaloids could be obtained by a similar method. The sodium and potassium derivatives of codeine and narcotine and the sodium derivative of cotarnine were obtained by boiling the alkaloids with the respective metals in benzene, and the calcium derivative of morphine was isolated from the solution of morphine in lime-water or from its alcoholic solution, prepared by titrating morphine with an excess of slaked lime in alcohol. Of the metallic derivatives, those of narcotine require special mention; there is no hydroxyl group present in the molecule, and there is no hydrogen atom attached to the nitrogen that could be displaced by the metals, as is generally represented to be the case with basic or quasi-basic nitrogenous organic compounds.

Sodium Codeine.

A mixture of 200 c.c. of benzene, 5 grams of freshly cut sodium, and 10 grams of powdered anhydrous codeine was boiled under reflux. At the beginning of the experiment, a very faint ammoniacal odour was perceived at the open end of the condenser, and this continued until the end of the operation. Within ten minutes the benzene turned brownish-yellow, and after half an hour it became opaque. After the mixture had boiled for ten hours, the pieces of sodium were covered with a thin layer of a reddish-brown substance, and the boiling was discontinued. On cooling, the contents of the flask set to a viscous mass like brown jelly, which was collected, pressed between filter paper, and kept

over night in a desiccator over sulphuric acid, when it dried to a brownish-yellow powder:

0.3537 gave 0.0800 Na_2SO_4 . $\text{Na}=7.32$.

$\text{C}_{18}\text{H}_{20}\text{O}_3\text{NNa}$ requires $\text{Na}=7.18$ per cent.

Sodium codeine is readily soluble in water, giving a brownish-yellow, turbid solution which does not become clear by filtration, but the turbidity disappears on the addition of dilute hydrochloric acid, and the colour is also considerably discharged. It is soluble in alcohol, but insoluble in ether, benzene, or chloroform, and is specifically lighter than the last solvent. The compound is slightly deliquescent; on exposure to the air, it absorbs moisture and becomes viscid, but when left in that condition for a long time it does not appear to change. Its aqueous solution does not give any precipitate with Mayer's reagent, but on acidifying the mixture, an immediate curdy, yellow precipitate is obtained.

Potassium Codeine.

Ten grams of dry powdered codeine were dissolved in 200 c.c. of benzene, and the solution was boiled with 10 grams of potassium as before. The potassium melted and formed smaller shining balls, around which a brisk evolution of gas took place. As in the former experiment, a faint ammoniacal odour was always perceived at the open end of the condenser. Within an hour the benzene gradually assumed a reddish-brown colour, and soon afterwards red crystals began to separate. The boiling was continued until a voluminous mass of crystals separated, which were collected, washed three times with boiling benzene, pressed between filter paper, and kept overnight in a desiccator over sulphuric acid. About 5 grams of the substance were powdered, added to 50 c.c. of benzene, and the mixture was gently boiled for five minutes. It was then filtered whilst hot, and the residue washed three times with boiling benzene to remove codeine, being finally pressed between filter paper and dried in a desiccator over sulphuric acid:

0.8000 gave 0.1590 K_2SO_4 . $\text{K}=11.88$.

$\text{C}_{18}\text{H}_{20}\text{O}_3\text{NK}$ requires $\text{K}=11.59$ per cent.

Potassium codeine dissolves in water, giving a clear solution; it is soluble in alcohol, sparingly so in chloroform, and insoluble in ether or benzene.

Sodium Narcotine.

Five grams of narcotine were boiled with 200 c.c. of benzene and 5 grams of clean sodium; a faint ammoniacal odour was per-

ceived, and the colour of the liquid became brown. After boiling for three daily periods of five hours each, some crystals were deposited, which were collected, washed with hot benzene, pressed between filter paper, and kept overnight in a desiccator, when a reddish-yellow powder was obtained:

0.4110 gave 0.7400 Na_2SO_4 . $\text{Na} = 5.82$.

$\text{C}_{22}\text{H}_{22}\text{O}_7\text{NNa}$ requires $\text{Na} = 5.41$ per cent.

Sodium narcotine is a non-deliquescent substance, readily soluble in water to a pale yellow, transparent solution, which does not produce any precipitate with Mayer's reagent, except on acidification. It is soluble in alcohol or chloroform, and almost insoluble in ether or benzene. Nothing could be extracted from its aqueous solution by benzene or ether. When the solution was boiled, however, a slight turbidity was observed, which increased on passing carbon dioxide; the precipitate was collected, washed, and dried, when it melted at 175° . Narcotine also separated in colourless, needle-shaped crystals when the solution was kept in an open flask for six or seven days, but the alkaloid was completely and readily recovered as a colourless, crystalline powder by dissolving the compound in ammonium chloride. It was collected, washed, dried, and recrystallised from benzene, when it melted at 173° and had all the properties of pure narcotine.

Potassium Narcotine.

In the preparation of other metallic derivatives, excess of the metals were used as a rule, but with the potassium derivative of narcotine considerable difficulty was experienced in obtaining the new compound free from unchanged metal. After a part of the reaction was completed, the molten potassium disintegrated into very small pieces, which were never completely separated from the derivative, but became entangled with the crystals of the new compound and did not settle down separately when cooled. To avoid this difficulty, excess of the alkaloid was employed, and the unchanged narcotine was removed by washing with benzene. Five grams of potassium and 40 grams of narcotine were boiled with 300 c.c. of benzene under reflux. Within an hour the potassium derivative began to be deposited as a brownish-yellow powder. The boiling was continued for twelve hours, during which period the usual faint ammoniacal odour was noticed; the mixture was filtered hot, and the precipitate washed five times with boiling benzene, care being taken to keep it covered with liquid, since the substance rapidly absorbs moisture, becoming nacreous,

and then cannot be filtered; the compound also undergoes slight decomposition. The washing with hot benzene, however, may be continued until the filtrate ceases to give any residue on evaporation. The substance was pressed between filter paper and dried in a desiccator over sulphuric acid:

0.1401 gave 0.0501 K_2SO_4 . $K=16.00$.

$C_{22}H_{21}O_7NK_2$ requires $K=15.90$ per cent.

Dipotassium narcotine is a bright yellow, crystalline powder readily soluble in alcohol, giving a turbid solution; it dissolves in chloroform, is sparingly soluble in benzene, and insoluble in ether. On shaking its aqueous solution with benzene, only a very small quantity of the alkaloid was extracted by the solvent, but when the mixture was shaken with an excess of ammonium chloride, the benzene dissolved almost the whole of the alkaloid. The benzene solution was separated, washed, dried by potassium carbonate, and evaporated, when there remained a non-crystalline residue melting at 160° . Consequently, the substance thus recovered is not pure narcotine, as was the case with the sodium derivative.

Sodium Cotarnine.

Cotarnine was prepared by oxidising narcotine with dilute nitric acid, a slight modification of the method described by Anderson (*Annalen*, 1853, **86**, 187) being used. A mixture of 70 c.c. of nitric acid (D 1.4) and 200 c.c. of water was cooled to 15° , 25 grams of crystallised narcotine were added, and the whole was shaken continuously until the alkaloid was completely dissolved, the solution being kept in a cool place overnight. The white crystals of opianic acid which had settled at the bottom were collected, and the cotarnine was precipitated from the filtrate by means of potassium hydroxide. The alkaloid was well washed, dried in a desiccator over sulphuric acid, and recrystallised from benzene, when it weighed 6.1 grams.

Ten grams of cotarnine, 5 grams of sodium, and 200 c.c. of benzene were heated under reflux; after four hours crystals began to separate, and the boiling was continued for six hours, when the mixture was set aside overnight for the complete precipitation of crystals. These were collected, washed three times with hot benzene, pressed between filter paper, and dried in a desiccator:

0.0130 gave 0.0115 Na_2SO_4 . $Na=28.0$.

$C_{12}H_{11}O_4NNa_4$ requires $Na=28.30$ per cent.

Tetrasodium cotarnine is a hygroscopic, bright yellow, crystalline powder, readily soluble in water, giving a clear solution, soluble

in alcohol or chloroform, sparingly so in ether, and practically insoluble in benzene. This compound showed a behaviour altogether different from that of the allied alkaloids in that its aqueous solution gave a precipitate with Mayer's reagent, the amount of which slightly increased on keeping the solution for a day or on acidifying the freshly prepared solution. When its saturated aqueous solution was treated with an excess of ammonium chloride, an immediate turbidity was observed, and on keeping overnight, a crystalline precipitate had formed. This was collected, washed, pressed between filter paper, and dried in a desiccator over sulphuric acid, when it melted at 132° .

Calcium Morphinate.

Morphine is well known to be soluble in lime-water, forming calcium morphinate, which was easily isolated by the following process. Thirty grams of pure morphine were triturated with 6 grams of pure calcium hydroxide, 100 c.c. of rectified spirit were added, the whole being well mixed for thirty minutes and then filtered. The pale brown filtrate was transferred to a shallow dish and kept in a desiccator over sulphuric acid; after two days, calcium morphinate separated as a shining, scaly, light powder. The product obtained by substituting water for alcohol was not so pure, and was much darker. The alcoholic product was completely dissolved by alcohol or water, whereas the other left a slight residue, and a clear solution was only obtained from it by filtration. Consequently, the alcoholic product was assumed to be pure:

0.2060 gave 0.0200 CaO. Ca = 6.93.

$(C_{17}H_{15}O_3N)_2Ca$ requires Ca = 6.58 per cent.

A quantity of the substance was dissolved in *N*/10 sulphuric acid, and the excess titrated with *N*/10-sodium carbonate, using methyl-orange as indicator.

0.5 required 32.6 c.c. of *N*/10-acid, whereas this weight of a compound of the above formula requires 33.11 c.c. of *N*/10-acid to neutralise both calcium and morphine.

Calcium morphinate is a brown, non-deliquescent powder readily soluble in water or alcohol, sparingly so in chloroform, and insoluble in ether or benzene. Its aqueous solution gives the usual precipitate of morphine with ammonium chloride, and with Mayer's solution it gives a precipitate only after acidification. It is readily decomposed by carbonic acid, calcium carbonate and morphine being precipitated.

The investigation is being extended to the metallic derivatives of other alkaloids and to the study of the constitution of the compounds described above.

The author desires to express his best thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of the investigation.

OPIMUM FACTORY,
CHAZIPORE, INDIA.

[Received, April 10th, 1917.]

XLI.—*Studies in Catalysis. Part IX. The Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

In previous papers of this series (compare T., 1916, 109, 796; 1917, 111, 457), expressions have been obtained, with the aid of the radiation hypothesis, for velocity constants and equilibrium constants as functions of temperature. In the expressions thus obtained, there occur certain proportionality factors which have to be determined by direct comparison with experiment. In the present paper an attempt is made to deal with the problem in a more complete manner by calculating velocity and equilibrium constants in terms of quantities, all of which have a definite physical meaning and may be determined, theoretically, without reference to the actual rate of the chemical reaction itself.

On the basis of statistical considerations, J. Rice (*Rep. Brit. Assoc.*, 1915, 397) has deduced an expression for the reaction velocity and velocity constant in the case of a unimolecular reaction, that is, the spontaneous decomposition of a single molecule. The assumption made by Rice is that the rate of such a reaction is determined by the rate at which the molecules become active in the physical sense. Active molecules, in unimolecular processes, have therefore no real existence. When, however, we deal with multimolecular reactions, it is conceivable that active molecules exist, the rate of the observed reaction depending on the number of collisions per second which take place between active molecules of the participating substances. The concept of active molecules

was first postulated by Arrhenius, but it is only within recent years that the differentiation between active and passive molecules has attained any degree of precision through the introduction of the concept of critical energy and critical increment. The most direct evidence of an experimental kind which we possess at the present time for the existence of active molecules is that afforded by the measurements of Baly and F. O. Rice (T., 1912, 101, 1475) in the case of the sulphonation of certain aromatic compounds. In this case, the ultimate chemical reaction is multimolecular, probably bimolecular. We may adopt therefore with some confidence the view that active molecules have a real existence in the case of multimolecular reactions. These active molecules differ from the remainder in respect of their internal energy, which is considerably greater than that possessed by an average molecule of the substance at the temperature in question. The fact that the critical energy is high means that only a very small fraction of the total molecules will be active at any moment.

In the case of a bimolecular reaction, such as the decomposition of hydrogen iodide in the gaseous state, the fractional number of hydrogen iodide molecules which exist in the active state may be calculated by the aid of the expression

$$N_a/N = e^{-E/RT} \dots \dots \dots (1)$$

where N_a denotes the number of active molecules, N the number of passive molecules or the total number of molecules (since N_a is very small compared with N); E is the critical increment reckoned per gram-molecule, that is, the amount of energy which one gram-molecule of the substance must absorb in order to make it reactive, and R and T have their usual significance. This expression is the familiar one obtained on the basis of statistical mechanics for the distribution of molecules in a field of force. The justification for its application to the present case is furnished by the following calculation of the velocity constant of decomposition of gaseous hydrogen iodide.

In Bodenstein's experiments (*Zeitsch. physikal. Chem.*, 1899, 29, 295), one gram-molecule was present in 22.4 litres. At 556° abs. the observed velocity constant was 9.42×10^{-7} , the unit of time being the minute. On expressing the time in seconds and the concentration in gram-molecules per litre, the velocity constant becomes 3.517×10^{-7} . This number represents the fraction decomposed per second at unit concentration.

We have now to calculate the velocity constant on the basis of the concept of active molecules, the equilibrium concentration of which is assumed to be given at all stages of the observed reaction

by equation (1). From the temperature-coefficient* of the reaction, it is calculated that the critical increment per gram-molecule is 22,000 cal. Hence, employing equation (1), it is found that the fraction of one gram-molecule which exists in the active state at 556° abs. is 2.218×10^{-9} . If there is one gram-molecule of hydrogen iodide present in 1 litre, then this number represents the fractional number of active molecules. Since there are 6.1×10^{23} molecules in one gram-molecule, the actual number of active molecules per litre is 1.35×10^{15} , or 1.35×10^{12} per c.c.

On the kinetic theory, the number of collisions per c.c. per second between like (active) molecules is given by the expression

$$\sqrt{2} \cdot \pi \cdot \sigma^2 \cdot u \cdot N_a^2$$

where N_a is the number of active molecules per c.c., u the mean velocity of translation per molecule, and σ the distance within which two molecules approach one another during a collision. Physical theory has not yet succeeded in defining σ with precision, beyond the fact that it is of the order of magnitude of the radius or diameter of the molecule. Such being the case, we shall take a mean value, 2×10^{-8} cm., and employ this in all cases examined. Naturally, this will introduce a certain error into the results, but its magnitude will not affect the general question of the verification of the method of treatment adopted.

In the case of hydrogen iodide at 556° abs., $u = 3.3 \times 10^4$ cm. per second. The value of N_a we have already calculated to be 1.35×10^{12} per c.c. Hence the number of collisions per c.c. per second between the active molecules is 1.065×10^{14} , or the number of collisions per litre is 1.065×10^{17} . At each collision between active molecules, two such molecules react. Hence the number of molecules of hydrogen iodide which react per second per litre is 2.13×10^{17} . Expressing this as a fraction of one gram-molecule, we obtain $2.13 \times 10^{17} / 6.1 \times 10^{23} = 3.5 \times 10^{-7}$. This should be the velocity constant of the reaction expressed in gram-molecules per litre per second. The observed value is 3.517×10^{-7} . The agreement is very satisfactory, especially in view of the possible error in σ . This calculation serves to substantiate the concept of active molecules defined in the above sense.

The foregoing calculation may be carried out in a somewhat different manner which leads directly to the differential equation expressing the reaction velocity. Thus the number of molecules which react per c.c. per second is given by:

$$2 \sqrt{2} \pi \sigma^2 u N_a^2.$$

* This is the most direct means of obtaining the critical increment. It may also be obtained from the position of the effective absorption band in the spectrum of the substance provided the data are available.

Hence the number of molecules which react per litre per second is given by:

$$2000 \sqrt{2\pi\sigma^2 u N_a^2}.$$

N_a is the number of active molecules per c.c. Hence the number of active molecules per litre is 1000 N_a . If N_0 be the number of molecules in one gram-molecule, the number of active gram-molecules per litre is 1000 N_a/N_0 . If we denote this by C_a , then $N_a = N_0 C_a/1000$, or $N_a^2 = N_0^2 C_a^2/10^6$. Hence the number of molecules which react per litre per second is:

$$2000 \sqrt{2\pi\sigma^2 u N_0^2 C_a^2}/10^{-6}.$$

The number of gram-molecules which react per litre per second is $1/N_0$ of the above quantity. That is, the number of gram-molecules which react per litre per second is

$$2000 \sqrt{2\pi\sigma^2 u N_0 C_a^2}/10^4.$$

From equation (1), it follows that $C_a = C e^{-E/RT}$, where C is the total concentration or number of gram-molecules of hydrogen iodide per litre. Hence the rate of the observed reaction is given by:

$$-dC/dt = 5.40 \times 10^{21} \cdot \sigma^2 \cdot u \cdot C^2 \cdot e^{-2E/RT}.$$

But the rate, $-dC/dt = k_{\text{obs.}} \cdot C^2$, where $k_{\text{obs.}}$ is the velocity constant experimentally determined. Hence, $k_{\text{obs.}}$ (in gram-molecules per litre, per second)

$$= 5.40 \times 10^{21} \cdot \sigma^2 \cdot u \cdot e^{-2E/RT} \quad \dots (2)$$

By making use of the concept of active molecules, we can calculate the velocity constants of decomposition of hydrogen iodide over the temperature range corresponding with Bodenstein's observations. The following table contains the calculated and observed velocity constants expressed in gram-molecules per litre per second.

Decomposition of Hydrogen Iodide.

T .	$u \times 10^{-4}$	Fraction of one gram-molecule in the active state = $e^{-E/RT}$.	$e^{-2E/RT}$.	k calculated [equation (2)].	k observed.
556°	3.30	2.218×10^{-9}	4.898×10^{-18}	3.5×10^{-7}	3.517×10^{-7}
575	3.356	2.704×10^{-9}	1.820×10^{-17}	1.319×10^{-6}	1.217×10^{-6}
629	3.510	2.244×10^{-8}	5.012×10^{-16}	3.890×10^{-5}	3.02×10^{-5}
647	3.559	3.656×10^{-8}	1.318×10^{-15}	10.23×10^{-5}	8.587×10^{-5}
666	3.612	5.970×10^{-8}	3.548×10^{-15}	2.768×10^{-4}	2.195×10^{-4}
683	3.657	8.995×10^{-8}	8.128×10^{-15}	6.421×10^{-4}	5.115×10^{-4}
700	3.702	1.337×10^{-7}	1.778×10^{-14}	1.422×10^{-3}	1.157×10^{-3}
716	3.744	1.905×10^{-7}	3.648×10^{-14}	2.87×10^{-3}	2.501×10^{-3}
781	3.912	6.918×10^{-7}	4.786×10^{-13}	4.04×10^{-2}	3.954×10^{-1}
1000	4.42	1.545×10^{-5}	2.371×10^{-10}	22.63	—

The agreement between the observed and calculated values is satisfactory. The number of active molecules per c.c. rises from 1.35×10^{12} at 556° abs. to 4.22×10^{14} at 781° abs. Further, it is seen that at 556° abs., when the total concentration is one gram-molecule per litre, the ratio

$$\frac{\text{number of effective collisions per c.c. per second}}{\text{total number of collisions per c.c. per second}} = \frac{1.065 \times 10^{14}}{2.18 \times 10^{14}} = 4.9 \times 10^{-13}.$$

By the term effective collision is meant, of course, the number of collisions between active molecules. This ratio is seen to be an exceedingly small quantity. This quantity may be called conveniently the 'chemical efficiency' of the reaction, since it denotes the number of chemically effective collisions expressed as a fraction of the total number of collisions in the same time. This quantity, as we would expect, increases rapidly with the temperature. Thus, at 781° abs., the chemical efficiency of the reaction considered is 4.8×10^{-13} . At a very high temperature, the upper limit of the efficiency, namely, unity, should be attained theoretically. This temperature must be such that the quantity $e^{-E/RT}$ shall be unity. At 2000° abs., the value of $e^{-E/RT}$ would be 3.9×10^{-3} , and therefore the number of active molecules per c.c., when one gram-molecule is present in one litre, is 2.38×10^{18} . The chemical efficiency is therefore 1.5×10^{-5} . We conclude, therefore, that over any temperature range amenable to experiment in the above reaction the chemical efficiency will be a small quantity.

Bodenstein (*loc. cit.*) has also measured the velocity of union of hydrogen and iodine, and has shown it to be a bimolecular reaction. From the temperature-coefficient, it is easily calculated that the sum of the critical increments per gram-molecule of hydrogen and of iodine is 40,000 cals. This quantity is the analogue of the term $2E$ in the case of the bimolecular decomposition of hydrogen iodide. The quantity 40,000 cals. is made up of two terms, namely, the respective increments of hydrogen and iodine, but at the present stage we do not know each of these terms separately. This is unnecessary, however, for the immediate object in view. It may be noted that the critical increment here referred to is not the critical increment of complete dissociation of hydrogen and of iodine into the atomic state. It will be shown later that the total energy necessary to effect complete dissociation of one gram-molecule of hydrogen and the same mass of iodine is (87,000 + 41,000), or 128,000 cals. The quantity, 40,000 cals., corresponds with a partial activation or polarisation of the hydrogen and iodine molecules sufficient to allow them to react on collision. The partly

activated molecules have a real existence, the system being quite analogous to the partly activated molecules of hydrogen iodide.

On the kinetic theory, the number of collisions per second per c.c. between two unlike molecules is given by the expression:

$$\pi \cdot \sigma^2 \cdot N_1 \cdot N_2 \cdot \sqrt{u_1^2 + u_2^2},$$

where σ is the average distance to which the molecules approach during a collision, u_1 and u_2 are the mean velocities of translation of the two kinds of molecules, and N_1 and N_2 are the number of active molecules of each kind present in unit volume. The value 2×10^{-8} is assigned to σ . Following the same line of argument as that employed in the deduction of equation (2), we find that the bimolecular velocity, expressed in gram-molecules per litre per second, is given by:

$$-dC/dt = 3.8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} \times C_{H_2} \cdot C_{I_2} \cdot e^{-40,000/RT}$$

or,

$$k_{\text{calc.}} = 3.8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} \cdot e^{-40,000/RT} \quad (2a)$$

The following table contains the values of the velocity constants calculated by means of equation (2a) and those observed by Bodenstein.

Union of Hydrogen and Iodine.

T abs.	$\sqrt{u_1^2 + u_2^2}$ $\times 10^{-4}$	$e^{-40,000/RT}$	k calculated by equation (2a).	k observed.
556°	26.5	1.862×10^{-16}	7.39×10^{-5}	4.44×10^{-5}
629	28.2	1.23×10^{-14}	5.19×10^{-3}	2.25×10^{-3}
666	29.0	7.24×10^{-14}	3.14×10^{-2}	1.415×10^{-2}
700	29.7	3.16×10^{-13}	14.0×10^{-2}	6.42×10^{-2}
781	31.4	6.31×10^{-12}	2.97	1.336

The agreement between observed and calculated values is moderate. The concordance is evidently limited mainly by the degree of approximation in the value taken for σ . In general, the theoretical basis upon which the calculations are founded may be regarded as justified.*

Stegmüller (*Zeitsch. Elektrochem.*, 1910, **16**, 85) has measured, by an electromotive force method, the equilibrium constant of the hydrogen iodide reaction at much lower temperatures than those with which Bodenstein's measurements correspond. By employing equations (2) and (2a), it should be possible to calculate the equilibrium constant at any temperature provided the gases do not deviate seriously from the perfect gas. The following table con-

* From the above data it is found that by setting $\sigma = 1.34 \times 10^{-8}$ cm. the calculated and observed values of the velocity constants become nearly identical. This value has been employed in the table dealing with Stegmüller's results.

tains the values so calculated and those obtained by Stegmüller. Stegmüller's values have been recalculated to give the equilibrium constant in the form $C_{H_2} \times C_{I_2}/C_{HI}^2$. The velocity constants are expressed in gram-molecules per litre per second.

Equilibrium Constant of the Hydrogen Iodide Reaction at Low Temperatures.

T abs.	Bimolecular velocity constant of decomposition (equation 2).	Bimolecular velocity constant of union (equa- tion 2a) ($\sigma = 1.34 \times 10^{-3}$)	Equilibrium constant calculated.	Equilibrium constant, Stegmüller.
304.6°	1.356×10^{-21}	2.51×10^{-18}	5.4×10^{-4}	11.9×10^{-4}
328.2	2.62×10^{-19}	3.0×10^{-16}	8.7×10^{-4}	20.3×10^{-4}
354.6	4.123×10^{-17}	2.98×10^{-14}	14×10^{-4}	38.3×10^{-4}

The calculated equilibrium constants are between one-half and one-third of the observed values. Closer agreement is obtained in other reactions, considered later. As illustrated in the above table, we are able to calculate with a moderate degree of accuracy the velocity constants of the opposing reactions, quantities which, owing to their exceedingly small magnitude over the range of temperature considered, could not be determined experimentally.

So far, we have dealt with reaction velocity in gaseous systems from the point of view of molecular statistics. We have now to consider it from the point of view of the radiation hypothesis.

We have seen already that the critical increment of the bimolecular decomposition of hydrogen iodide is 22,000 cal. per gram-molecule. On the radiation hypothesis, this energy is supplied by $N_0 h \nu$ quanta, where N_0 is the number of molecules in one gram-molecule, h is Planck's constant, and ν the frequency of the effective radiation. It is easily calculated that the required frequency is 2.33×10^{14} , or $\lambda = 1.3 \mu$, in round numbers. If the above reasoning is correct, gaseous hydrogen iodide should exhibit an absorption band at this wave-length, especially if the gas be heated. The author is unaware of any experimental data bearing on this point.

On the basis of the quantum theory, Planck has considered the problem of the relation of emission to non-emission by an oscillator (compare Planck, "Theory of Heat Radiation," English trans., p. 164). According to Planck, the ratio of the probability that no emission takes place to the probability that emission does take place is proportional to the radiation density u_ν of the frequency ν . The ratio is given by the expression $p \cdot u_\nu$. The factor p is shown to be identical with the expression $c^3/8\pi h \nu^3$, where c is

the velocity of light in a vacuum and n the refractive index of the system for the frequency ν . For gaseous systems, n is practically unity. It will be observed that the probability that no emission takes place is inversely as the cube of the frequency. So long as no emission takes place, the energy of the oscillator, and therefore of the whole atom or molecule containing one or more oscillators, remains high. Such a molecule will correspond with an active one in the chemical sense. It is reasonable, therefore, to apply Planck's principle to a case such as the decomposition of hydrogen iodide and write,

$$\frac{\text{the number of chemically active molecules in existence}}{\text{the number of passive molecules}} = p \cdot u_{\nu}$$

Since the number of active molecules is exceedingly small, the number of passive molecules is practically identical with the total number present, or, employing the symbols used previously,

$$Na/N = p \cdot u_{\nu}$$

This relation expresses the fact that the higher the radiation density the greater is the number of molecules in the active state. We may also write this expression in the form:

$$\text{Fraction of one gram-molecule in the active state} = pu_{\nu}$$

Further, for the short infra-red, visible and ultra-violet regions,

$$u_{\nu} = \frac{8\pi h n^3 \nu^3}{c^3} e^{-N_0 h \nu / RT},$$

Hence,

$$p \cdot u_{\nu} = e^{-N_0 h \nu / RT}$$

or the fraction of one gram-molecule in the active state is $e^{-N_0 h \nu / RT}$. But $N_0 h \nu = E$, the critical increment per gram-molecule. Hence the fraction of one gram-molecule in the active state $= e^{-E/RT}$, which is the expression already obtained on the statistical mechanical basis, and verified by the experimental data. We are justified, therefore, in making the assumption that the chemically active fraction of each gram-molecule of hydrogen iodide is given by the expression $p \cdot u_{\nu}$. This should hold good for any substance which reacts in the bimolecular, or in general the multimolecular manner. It is only in such cases that active molecules have any real existence. In the case of unimolecular reactions, active molecules do not exist as such.

In a bimolecular reaction of the type considered, if C denotes the total number of gram-molecules in a given volume, say 1 litre. then the number of active gram-molecules in the same volume may be expressed by

$$C \cdot p \cdot u_{\nu} \text{ or } C \cdot e^{-N_0 h \nu / RT} \text{ or } C \cdot e^{-E/RT}$$

On the purely kinetic basis, we have seen that the rate of reaction between like molecules in a bimolecular reaction per litre per second is:

$$-dC/dt = 5.4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot C^2 e^{-2E/RT}.$$

The term $C^2 \cdot e^{-2E/RT}$ is evidently identical with $C^2 \cdot p^2 \cdot u^2$, so that the rate of reaction may be written,

$$-dC/dt = 5.4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot p^2 \cdot C^2 \cdot u^2.$$

That is, the rate of the observed bimolecular reaction depends on the square of the radiation density, a conclusion which is in agreement with the assumption made in earlier papers in connexion with bimolecular reactions. The advantage of the present mode of treatment is, however, that all the factors which go to make up the observed velocity constant are calculable quantities. It is evident that the observed velocity constant, expressed in gram-molecules per litre per second, for a bimolecular reaction involving like molecules is given by:

$$k_{\text{obs}} = 5.4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot p^2 \cdot u^2,$$

or

$$k_{\text{obs}} = 5.4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot e^{-2N_h \nu / RT}.$$

It is obvious that differentiation of this expression with respect to temperature yields the well-known Arrhenius equation as a first approximation.

In a bimolecular reaction such as that considered, the function of the radiation of the absorbable type is to maintain a certain number of molecules in the chemically active state, a state which means high energy content. The number of active molecules at any moment is the difference between their rate of production and their rate of disappearance. Their rate of disappearance is due to retransformation of some into the passive state, and at the same time the transformation of others in the ordinary chemical sense into the resultants. It is simply the number of active gram-molecules *in existence* at any moment which has been written as $C \cdot p \cdot u$. The actual rate of production of active molecules per second is a quantity necessarily much greater than this. An attempt will now be made to estimate this rate.

In the case of hydrogen iodide at a concentration of one gram-molecule per litre at 556° abs., we have seen that the number of active molecules maintained by the radiation in the active state per litre is 1.35×10^{15} . The number of active molecules which react per second per litre is 2.13×10^{17} . If we denote by R_1 the rate of production of active molecules per second per litre, by R_2 the rate of chemical reaction (2.13×10^{17}), and by R_3 the rate at

which active molecules are retransformed into passive molecules per litre per second, we have the relation:

$$R_1 - (R_2 + R_3) = 1.35 \times 10^{15}.$$

In order to maintain the active molecules and allow for the rate of the observed reaction, the minimum rate of production of active from passive molecules is $> 2.13 \times 10^{17}$. The true rate may, however, be much greater than this lower limit. It is evident that the rate of production of active molecules must depend on the radiation density u , but it is evident the rate is not given by the expression $N_0 \cdot p \cdot u$, for this would only account for a production of 1.35×10^{15} active molecules per second from one gram-molecule. A quantity having a higher numerical value than $N_0 \cdot p \cdot u$ is required. The terms N_0 and u would be expected to remain unaltered, and we are limited to some function of p . It will be shown later, in connexion with the dissociation of iodine, bromine, and chlorine, that the experimental values can be accounted for if we assume provisionally that the required function is $10^3 p^*$. With this assumption, the rate of production of active molecules from one gram-molecule is $N_0 \cdot 10^3 \cdot p^2 \cdot u$. Since u itself can be written as $\frac{1}{p} e^{-N_0 h \nu / RT}$, our assumption means that the rate of production of active molecules is given by $10^3 \cdot N_0 \cdot p \cdot e^{-N_0 h \nu / RT}$, or $10^3 \cdot N_0 \cdot p \cdot e^{-E/RT}$. This expression should be the correct one for any spontaneous unimolecular reaction, for in such a case the process of activation is identical with the chemical reaction. That is, the velocity constant of a unimolecular reaction should be given by:

$$k_{\text{obs.}} = 10^3 \cdot p \cdot e^{-E/RT}$$

We shall now apply this expression to the calculation of the rate of production of active molecules of hydrogen iodide. The term p is given by $c^3/8\pi h n^3 \nu^3$, and since, for the process considered, $E = N_0 h \nu = 22,000$ cal. per gram-molecule, the frequency ν must be 2.33×10^{14} . Further, the system is gaseous, and therefore the refractive index is practically unity. Hence $p = 1.307 \times 10^{13}$. Hence the number of active molecules produced per second from one gram-molecule of hydrogen iodide at 556° abs. $= 6.1 \times 10^{22} \times 1.307 \times 10^{13} \times 2.218 \times 10^{-9} = 1.768 \times 10^{23}$. If we divide this number by 6.1×10^{23} , we obtain the fraction of one gram-molecule activated per second. A rate of this magnitude is quite possible in the sense that it is sufficient to account for the observed rate of the

* This function will be dealt with in a later paper, in which an alternative expression, having a similar numerical value, but possessing a more precise physical significance, will be given.

bimolecular reaction, and likewise for the maintenance of the free active molecules. Since the rate of production of active molecules is considerably greater than the sum of the two effects just mentioned, it follows that the rate at which active molecules are re-transformed into passive is likewise of the order 10^{12} . If these extremely high opposing velocities exist, we are led to the conclusion that the equilibrium between active and passive molecules is attained practically instantaneously. This is in agreement with experience, but, of course, such evidence is very inconclusive. Quantitative evidence is furnished by the calculation of the equilibrium constant in the case of the dissociation of iodine, bromine, and chlorine. This will be considered later.

Whilst the ordinary thermal decomposition of hydrogen iodide is a bimolecular process, Bodenstein has shown (*Zeitsch. physikal. Chem.*, 1907, **61**, 447) that the photochemical decomposition is unimolecular. In this case, the process is the decomposition of hydrogen iodide molecules into atoms of hydrogen and iodine. This is effected by short waves. That is, the process of completely decomposing the hydrogen iodide molecule is a much more difficult one to carry out and requires a greater size of quantum than is required simply to displace the atoms somewhat with respect to one another inside the hydrogen iodide molecule, thereby permitting the bimolecular process to take place. In Bodenstein's experiments on the photochemical decomposition, the hydrogen iodide was exposed to bright sunlight in glass vessels. Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 889) find that hydrogen iodide is decomposed by blue or violet light. More precise knowledge is wanting, but it is evident that the active wave-length is of the order $450 \mu\mu$, or $\nu = 6.66 \times 10^{14}$. That is, the critical increment E' per gram-molecule of hydrogen iodide for the unimolecular decomposition is 63,000 cal. in round numbers. It will be shown later that a more exact value for this quantity is 66,000 cal. This is just three times the increment for the bimolecular reaction. The bimolecular reaction takes place, therefore, more readily, since a molecule will oftener possess the energy corresponding with E than the energy corresponding with E' . This unimolecular process must take place, however, as a thermal effect along with the bimolecular process, for, at any temperature, the radiation density, even at $\nu = 7.0 \times 10^{14}$, cannot be entirely wanting. Since, however, the radiation density diminishes rapidly as the frequency increases from the short infra-red into the ultra-violet, the unimolecular reaction, compared with the bimolecular, will remain negligible until very high temperatures are reached. On the basis of the considerations already developed, it is quite possible to calculate what this uni-

molecular decomposition velocity amounts to at any temperature. Thus, the rate of unimolecular decomposition of hydrogen iodide per gram-molecule is given by $10^3 \cdot N_0 \cdot p \cdot e^{-66,000/RT}$, where $p = 4.66 \times 10^{11}$. At 556° abs., this rate should be 3.12×10^{12} molecules per second when one gram-molecule is present initially. Hence the unimolecular velocity constant $= 10^3 \cdot p \cdot e^{-66,000/RT}$ is 5.1×10^{-12} . It will be observed that this is a small quantity compared with the bimolecular velocity constant (3.5×10^{-7}) under the same conditions. At 781° abs., the unimolecular velocity constant is 1.54×10^{-4} , whilst the bimolecular constant is 4.0×10^{-2} . The conclusion that the unimolecular decomposition is small compared with the bimolecular over the range examined by Bodenstein (556 — 781° abs.) is in agreement with the fact that the bimolecular formula holds good. We can easily calculate the bimolecular constant at 1000° abs. by the methods already employed at lower temperatures, the value obtained being 22.63. At the same temperature, the unimolecular velocity constant is calculated to be 1.73. At 1200° abs., the unimolecular constant is 435, whilst the bimolecular is 998. It is evident, therefore, that at a temperature somewhat above 1200° abs., the two types of decomposition will occur at the same rate. At this temperature, therefore, the bimolecular formula would be expected to break down.

We now turn to the consideration of unimolecular dissociation, such as that of iodine in the gaseous state into atoms. From the known behaviour of nascent atoms, it may be inferred that their normal state in respect of energy content is sensibly identical with the critical state, so that the exponential term in equation (2) containing the critical increment reduces to unity. Let C_u denote the equilibrium concentration of undissociated molecules of iodine expressed in gram-molecules per litre, and C_i the equilibrium concentration of the iodine atoms in the same units. The rate at which the molecular species dissociates is then given by $C_u \cdot 10^3 \cdot p \cdot e^{-N_0 h \nu / RT}$ or $C_u \cdot 10^3 \cdot p \cdot e^{-E/RT}$. In an earlier paper (T., 1917, 111, 1086), the value 41,000 cal., per gram-molecule, has been assigned to the critical increment of iodine. The corresponding frequency ν is 4.3×10^{14} , or $\lambda = 700 \mu$. Hence $p = c^3 / 8\pi h \nu^3 = 2.08 \times 10^{12}$. At $T = 1073$ ($t^\circ = 800^\circ$), the term $e^{-E/RT} = 4.385 \times 10^{-9}$. Hence the rate of dissociation, expressed in gram-molecules per litre per second, is $C_u \times 10^3 \times 2.08 \times 10^{12} \times 4.385 \times 10^{-9} = 9.16 \times 10^6 C_u$. The number 9.16×10^6 is the unimolecular velocity constant of dissociation. The rate at which the atoms combine is given by the total collision frequency, for in the case considered, the atoms are all active and every collision is effective. Since there are C_i gram-atoms per litre, the actual number of atoms per c.c. is

$C_i \times 6.1 \times 10^{30}$. The collision frequency per c.c. per second is $\sqrt{2} \cdot \pi \cdot u \cdot \sigma^2 \cdot C_i^2 \times 37.2 \times 10^{40}$. The average velocity of translation u of one iodine atom at 1073° abs. is 4.6×10^4 cm. per second. Taking σ as 2×10^{-8} cm., the number of collisions per c.c. per second is $3.031 \times 10^{81} \cdot C_i^2$. The number of atoms which combine is just twice this quantity, namely, $6.062 \times 10^{81} \cdot C_i^2$. Hence the number of gram-atoms which combine per second per litre is $9.94 \times 10^{10} \cdot C_i^2$. Alternatively, using equation (2) and writing the exponential term as unity, we arrive at the same result. It follows that $C_i^2/C_u = 9.16 \times 10^6 / 9.94 \times 10^{10} = 9.2 \times 10^{-5}$. Bodenstein and Starck (*Zeitsch. Elektrochem.*, 1910, **16**, 961) have measured the equilibrium constant, C_i^2/C_u , at 1073° abs., with the concentration expressed in gram-molecules per litre, the value obtained being 1.29×10^{-4} . The calculated equilibrium constant agrees well with the observed value. Again, consider the dissociation at 1473° abs. The value of $e^{-E/RT}$ is 8.166×10^{-7} . Hence the rate of dissociation in gram-molecules per second is

$$2.08 \times 10^{15} \times 8.166 \times 10^{-7} C_u.$$

From equation (2), taking σ as 2×10^{-8} and $u = 5.38 \times 10^4$, we get for the rate of union of the atoms, expressed in gram-atoms per litre per second, the value $1.14 \times 10^{11} \times C_i^2$. Hence

$$C_i^2/C_u = 1.699 \times 10^9 / 1.14 \times 10^{11} = 1.49 \times 10^{-2}.$$

The observed equilibrium constant is 1.02×10^{-2} .

The foregoing considerations, which are based partly on molecular statistics and partly on the quantum theory of radiation, allow us to calculate with a moderate degree of precision not only the equilibrium constant of a dissociation of a molecule into atoms (a quantity which is amenable in general to experimental determination), but likewise the separate velocity constants which, owing to their great magnitude, cannot be measured directly. The table on p. 484 contains the values of the equilibrium constants and the velocity constants in the above units for the dissociation of iodine over the range of temperature investigated by Bodenstein and Starck.

The agreement between the calculated and observed equilibrium constants is satisfactory. This affords considerable support for the assumptions made as regards the velocity constants. It may be pointed out that the term $e^{-E/RT}$ in this case does *not* represent the number of the active molecules of molecular iodine. No active molecules exist apart from the atoms. The conditions obtaining are quite distinct from those met with in the case of the bimolecular decomposition of hydrogen iodide.

Bodenstein (*Zeitsch. Elektrochem.*, 1916, **22**, 327) has measured

Dissociation of Iodine.

t°	T abs.	$e^{-E/RT}$	Mean velocity of transition of an iodine atom at t° per sec. $\times 10^{-4}$.		Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of recombination.	Equilibrium constant (calculated).	Equilibrium constant (observed).
			4.385×10^{-9}	4.6	9.16×10^8	9.94×10^{10}	9.2×10^{-2}	1.29×10^{-4}
800	1,073°			4.6				
900	1,173	2.266×10^{-8}		4.83	4.71×10^7	1.04×10^{11}	4.5×10^{-4}	4.82×10^{-4}
1,000	1,273.	8.995×10^{-8}		5.053	1.87×10^8	1.08×10^{11}	1.7×10^{-2}	1.88×10^{-2}
1,100	1,373	2.944×10^{-7}		5.24	6.12×10^8	1.13×10^{11}	5.4×10^{-2}	4.37×10^{-2}
1,200	1,473	8.166×10^{-7}		5.38	1.69×10^9	1.14×10^{11}	1.49×10^{-2}	1.02×10^{-2}

the dissociation constant of gaseous bromine between 800° and 1200°. He finds that the equilibrium constant, expressed in partial pressure terms, is given by the expression:

$$\log K_p = -10100/T + 1.75 \log T - 0.000409T + 4.726 \times 10^{-8}T^2 + 0.548.$$

Further details are not given in the abstract, which alone is available. At 1000° abs., this expression gives $\log K_p = 5.336$, whence the equilibrium constant K_c , expressed in gram-molecules per litre, is 2.64×10^{-7} .

An attempt will now be made to calculate this equilibrium constant. The critical increment E per gram-molecule of bromine is not known with accuracy (compare T., 1917, 111, 1086). It may be taken to be of the order 50,000 cal. The corresponding frequency $\nu = 5.3 \times 10^{14}$. Hence $p = 1.1 \times 10^{12}$ and

$$e^{-E/RT} = 1.175 \times 10^{-11}.$$

At the equilibrium point, the rate of dissociation of the bromine molecules is $10^3 \cdot p \cdot C_u \cdot e^{-E/RT} = 10^3 \times 1.1 \times 10^{12} \times 1.175 \times 10^{-11} \times C_u = 1.29 \times 10^4 C_u$, where 1.29×10^4 is the calculated unimolecular velocity constant of decomposition and C_u is the number of gram-molecules per litre. In dealing with the union of the atoms, we shall again make the assumption that the atoms are all active. At 1000° abs., the average speed u of a bromine atom is 5.6×10^4 cm. per second. Setting $\sigma = 2.0 \times 10^{-8}$ cm., and employing equation (2), we obtain for the rate of union of the atoms per second per litre the value $1.21 \times 10^{11} C_i^2$, where the numerical coefficient is the bimolecular velocity constant. The equilibrium constant is therefore given by $C_i^2/C_u = 1.29 \times 10^4 / 1.21 \times 10^{11} = 1.0 \times 10^{-7}$. This agrees satisfactorily with the observed value when we consider the possible error in σ and in E .*

The dissociation of chlorine has been measured by Pier (*Zeitsch. physikal. Chem.*, 1908, 62, 417), but the values appear to be much less accurate than those of Bodenstein in the case of bromine and iodine. Thus, the heat of the reaction when calculated from successive values of the equilibrium constant varies in quite an unexpected manner with the temperature. As the possibility of error seems to be less in the higher temperature range, we shall restrict ourselves to this region. Thus, at 1940° abs., the observed degree of dissociation of chlorine is 0.0157, the pressure being 0.5 atmosphere. Hence $K_c = x^2/(1-x)V = 7.8 \times 10^{-7}$. The critical increment of chlorine is taken to be 86,000 cal. per gram-molecule

* In the paper referred to, E for bromine was taken to be 57,000 cal. per gram-molecule. Employing the value 50,000 cal., the calculated heat of formation of potassium bromide is in rather better agreement, and the heat of formation of silver bromide in rather worse agreement with the corresponding observed value than are the numbers given in the former paper.

(compare T., 1917, 111, 1086). Hence at 1940° abs., $e^{-E/RT} = 2.014 \times 10^{-10}$. The frequency $\nu = 9.1 \times 10^{14}$. Hence $p = 2.2 \times 10^{11}$. At the equilibrium point, the rate of dissociation of chlorine is consequently $4.43 \times 10^4 C_u$, where 4.43×10^4 is the unimolecular velocity constant expressed in gram-molecules per second. The average speed u of a chlorine atom at 1940° abs. is 8.3×10^4 cm. per second. Taking σ as 2.0×10^{-8} cm., and using equation (2), we obtain, for the rate of union of the atoms, $1.793 \times 10^{11} C_i^2$, the velocity constant being expressed in gram-molecules per litre per second. Hence the equilibrium constant, C_i^2/C_u should be $4.43 \times 10^4 / 1.793 \times 10^{11}$, or 2.47×10^{-7} . It will be seen that the calculated and observed values of the equilibrium constant are of the same order of magnitude. The results obtained in the case of the three halogens, iodine, bromine, and chlorine, afford a considerable amount of evidence in favour of the theoretical treatment employed.

In the type of reaction just considered, namely, the dissociation of a molecule into atoms in the gaseous state, the position of equilibrium is given by the relation:

$$10^3 \cdot p \cdot e^{-E/RT} \cdot C_u = 5.40 \times 10^{21} \cdot \sigma^2 \cdot u \cdot C_i^2 \quad (3)$$

or

$$K = C_i^2/C_u = \frac{10^3 p \cdot e^{-E/RT}}{5.40 \times 10^{21} \cdot \sigma^2 \cdot u}$$

where the concentration is expressed in gram-molecules per litre. In a gaseous system p may be written as $1.6 \times 10^{56}/\nu^3$, where ν is the frequency of the radiation responsible for the dissociation process. For a given substance, ν is a constant independent of temperature so long as the mechanism of the process remains the same. We can write the above expression in the form:

$$\log K = -E/RT - \log u + \log 10^3 \cdot p / 5.40 \times 10^{21} \times \sigma^2.$$

The final term on the right-hand side is analogous to the integration constant which occurs in the thermodynamic treatment of mass-action equilibrium. In the present case, however, the final term is calculable quite apart from the reaction itself. On differentiating the above expression with respect to temperature, we obtain:

$$d \log K / dT = E/RT^2 - d \log u / dT.$$

The mean velocity of translation of an atom (which has been taken as practically identical with the root-mean-square-velocity) is proportional to the square root of the absolute temperature, u being given by the expression $\sqrt{3RT/M}$, where M is the gram-molecular weight of the atom. Hence

$$d \log K / dT = (E - 1/2 \cdot RT) / RT^2.$$

The term $(1/2)RT$ is, in general, small compared with E , and therefore the critical increment in the case of reactions of the above type is practically identical with the heat of dissociation at constant volume. This is the assumption which has been made in the foregoing treatment. If $-Q_v$ denotes the heat absorbed at constant volume per gram-molecule dissociated, we obtain the van't Hoff isochore from the above expression. For the type of reaction considered, the exact relation between the critical increment and the heat of the reaction is given by:

$$-Q_v = E - 1/2 \cdot RT \quad . \quad . \quad . \quad . \quad (4)$$

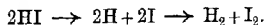
We are now in a position to deal with the dissociation of hydrogen. Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 417) finds that the heat of dissociation at constant volume at 3000° abs. is 84,000 cal. per gram-molecule. Hence, from equation (4), we obtain 87,000 cal. as the critical increment per gram-molecule of hydrogen. The corresponding frequency is 9.21×10^{14} , or $\lambda = 325 \mu$. Hence $p = 2.04 \times 10^{11}$. At 2000° abs., $e^{-E/RT} = 3.055 \times 10^{-10}$. Hence the rate of dissociation $= 10^3 \cdot p \cdot e^{-E/RT} \cdot C_u = 6.23 \times 10^4 C_u$. At 2000° abs., u for one hydrogen atom is 7.1×10^5 cm. per second. Taking $\sigma = 2 \times 10^{-8}$ cm., and using equation (2), the rate of union of hydrogen atoms, assuming all the atoms active, is $1.53 \times 10^{12} C_1^2$, the velocity constant being expressed in gram-atoms per litre per second. Hence the equilibrium constant is 4.07×10^{-8} . The degree of dissociation of hydrogen as determined by Langmuir is 0.0033 at 2000° abs. and under one atmosphere's pressure. Hence Langmuir's equilibrium constant, expressed in concentration terms, is 6.6×10^{-8} . This agrees fairly well with the calculated value. The main cause of the discrepancy is probably the fact that in the case of the hydrogen atom, σ is less than 2×10^{-8} cm. If we set $\sigma = 1.57 \times 10^{-7}$ cm., the two values of the equilibrium constant become identical. This value of σ is used in the following table, which contains the values of K obtained by Langmuir and those obtained by the above method of calculation.

Dissociation of Hydrogen.

T abs.	u in cm. per sec. $\times 10^{-5}$	Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of union.	Equilibrium constant, calculated.	Equilibrium constant, Langmuir.
1,500°	6.15	41.66	8.2×10^{11}	5.1×10^{-11}	4.6×10^{-11}
2,000	7.1	6.23×10^4	9.4×10^{11}	$[8.6 \times 10^{-8}]$	6.6×10^{-8}
2,500	7.95	4.98×10^6	1.1×10^{12}	4.7×10^{-6}	5.1×10^{-6}
3,000	8.66	9.26×10^7	1.2×10^{12}	8.0×10^{-5}	7.0×10^{-5}
3,500	9.37	7.46×10^8	1.3×10^{12}	6.0×10^{-4}	6.1×10^{-4}
4,000	10.0	3.58×10^9	1.33×10^{12}	2.7×10^{-3}	2.9×10^{-3}

The agreement throughout is satisfactory. It should be observed, however, that both series of K values are dependent on the numerical value for the heat effect, namely, 84,000 cal. at constant volume. This quantity has been verified approximately by Isnardi (*Zeitsch. Elektrochem.*, 1915, **21**, 405).

The following considerations also afford some support in favour of Langmuir's value for Q_v . We have seen that when hydrogen iodide decomposes in the *unimolecular* manner, the critical increment E' is approximately 63,000 cal. per gram-molecule. Let us suppose that two gram-molecules decompose in this manner, not in the ordinary bimolecular manner. That is, we have the reactions:



This will be referred to as the 'atomic' process. Although this is formally the same as the ordinary bimolecular process, the actual mechanism, involving as it does the formation of free atoms, is different, for in the bimolecular process we deal only with a polarisation or partial activation of each of the molecules H_2 , I_2 , and HI , a process which requires much less energy to reach the respective critical states than is required for the actual dissociation of each molecular species into atoms. Every chemical process, occurring spontaneously, follows the path of least resistance, that is, the path involving minimal critical increments. Hence the atomic process referred to is not the naturally occurring one. Since, however, the chemical change as a whole is the same in the two cases, the total heat effect must be the same. The heat absorbed when two gram-molecules of hydrogen iodide decompose is 4000 cal. approximately. Applying the expression developed and tested in former papers, namely,

$$\text{heat evolved} = (E_{\text{reactants}} - E_{\text{products}}),$$

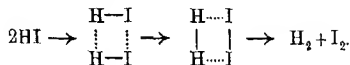
to the above atomic process, we obtain:

$$-4000 = E_{\text{H}_2} + E_{\text{I}_2} - 2E'_{\text{HI}}.$$

The symbol E_{I_2} , which is the critical increment of dissociation of iodine into its atoms, has the value 41,000 cal. per gram-molecule. $2 \times E'_{\text{HI}} = 2 \times 63,000$ cal. Hence the quantity E_{H_2} , which denotes the critical increment of dissociation of one gram-molecule of hydrogen into its atoms, has the value 81,000 cal. This should be sensibly identical with the heat absorbed in the dissociation of hydrogen. It is seen to be in fair agreement with Langmuir's value. The source of the discrepancy is due mainly to error in the value of E'_{HI} , which we have taken to be 63,000 cal. per gram-molecule on the basis of the rather qualitative statement

made by Berthelot and Gaudechon that hydrogen iodide is decomposed by blue or violet light. If we take the critical increment of hydrogen, in respect of dissociation into atoms, to be 87,000 cal. per gram-molecule (the value which has been employed in the compilation of the above table), it follows from a consideration of the atomic process of the decomposition of hydrogen iodide that E'_{HI} should be 66,000 cal., this being the quantity required to dissociate one gram-molecule of the substance into free atoms of hydrogen and iodine. From what has been said, this may be regarded as a more exact value of the critical increment of unimolecular decomposition than the value 63,000 cal. Certain conclusions have been drawn from this as regards the relative speeds of the unimolecular and bimolecular decompositions of hydrogen iodide in an earlier part of this paper. A further conclusion is that gaseous hydrogen iodide, when heated, should exhibit an absorption band in the region of $\nu=7 \times 10^{14}$, or $\lambda=429 \mu$. The author is unaware of any measurements in this connexion.

The decomposition of hydrogen iodide is particularly interesting, because it is one that is capable of occurring in two distinct ways, namely, the unimolecular and the bimolecular, and, if the previous considerations be accepted, we have fairly complete information regarding the mechanism of both. In the case of the ordinary bimolecular decomposition of hydrogen iodide, the critical increment E per gram-molecule is 22,000 cal. This is just one-third of the critical increment E' , 66,000 cal., which is required for the complete dissociation of the molecule into free atoms. The ordinary bimolecular process occurs, therefore, with much greater ease, that is, at lower temperatures, than does the unimolecular process. The bimolecular process involves, therefore, a certain separation or polarisation of the atoms in the molecule, but not their complete separation. The bimolecular process may be represented in the following manner, in which an additive compound is formed:



The total amount of energy required to activate two gram-molecules of hydrogen iodide in this manner is 44,000 cal.

In conclusion, we may collect together the various numerical values for the critical increments of the substances dealt with in the present paper.

Substance (gaseous).	Critical increment in cal. per gram-molecule.	Reaction involving the critical increment of the previous column.
Hydrogen iodide	22,000	$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ ordinary bimolecular reaction.
Hydrogen iodide	66,000	$\text{HI} \rightarrow \text{H} + \text{I}$ unimolecular reaction, identical with the photochemical decomposition.
Hydrogen	87,000	$\text{H}_2 \rightarrow 2\text{H}$.
Iodine	41,000	$\text{I}_2 \rightarrow 2\text{I}$.
Bromine	50,000	$\text{Br}_2 \rightarrow 2\text{Br}$.
Chlorine	86,000	$\text{Cl}_2 \rightarrow 2\text{Cl}$.

Summary.

(1) The observed rate of a unimolecular reaction is identical with the rate at which the molecules pass from the passive to the active state per second. The active state differs from the passive in respect of internal energy. The activation is ascribed to the radiation density of the absorbable radiation. In unimolecular reactions, active molecules have no real existence. They are, in fact, the resultants of the reaction. The critical increment E , that is, the quantity of energy which must be added to an average gram-molecule to raise its energy content to the critical state, is given by the expression $N_0 h \nu$, where h is Planck's constant, ν the frequency of the absorbable radiation, and N_0 the number of molecules in one gram-molecule. This statement is simply Einstein's law of the photochemical equivalent.

If the concentration of the decomposing substance is C , the provisional expression for the rate of decomposition in a unimolecular process is:

$$-dC/dt = 10^3 \cdot p \cdot C \cdot e^{-E/RT},$$

where $p = c^3/8\pi h n^3 \nu^3$, c being the velocity of light in a vacuum and n the refractive index of the system for the frequency ν . In the case of gaseous systems, $n=1$ very nearly, and $p=1.6 \times 10^{56}/\nu^3$. It follows that the observed velocity constant of a unimolecular process is given by:

$$k_{\text{obs}} = 10^3 p \cdot e^{-E/RT}.$$

Alternatively, the rate of unimolecular decomposition is given by:

$$-dC/dt = 10^3 \cdot p^2 \cdot C u_\nu,$$

where u_ν is the radiation density of the effective frequency ν , the radiation density being determined by the temperature of the system.

(2) The rate of a bimolecular reaction is identical with the

number of collisions which occur per second between the active molecules. As already pointed out in the case of *unimolecular* reactions, active molecules have no real existence. In bimolecular and multimolecular reactions generally, active molecules exist, their rate of formation being very much greater than their rate of collision, which latter term defines the observed rate of reaction. The number of active molecules in existence at any moment is proportional to the radiation density. In multimolecular reactions, the fraction of one gram-molecule existing in the active state is given on the basis of molecular statistics by the expression $e^{-E/RT}$, where E is the critical increment per gram-molecule. The fraction of one gram-molecule existing in the active state is given on the radiation basis by pu_v , which is identical with $e^{-N_0 h\nu/RT}$ and therefore with $e^{-E/RT}$. If C is the total concentration in gram-molecules per litre, the number of active gram-molecules per litre is $C \cdot e^{-E/RT}$. The number of "effective" collisions which occur in a gaseous system between like molecules (such as molecules of hydrogen iodide) per c.c. per second is given on the molecules kinetic theory by the expression,

$$\sqrt{2} \cdot \pi \cdot u \cdot \sigma^2 \cdot (\text{number of active molecules per c.c.})^2,$$

where u is the average velocity of translation of a molecule at the temperature considered and σ is the range of approach of two molecules during a collision. At each collision between active molecules, two molecules react. Hence the rate of reaction in a bimolecular process between like molecules occurring in the gaseous state is given by:

$$-dC/dt = 5.40 \times 10^{31} \cdot u \cdot \sigma^2 \cdot C^2 \cdot e^{-E/RT}.$$

Alternatively, since $e^{-2E/RT} = p^2 \cdot u_v^2$, the rate of reaction may be written:

$$-dC/dt = 5.40 \times 10^{31} \times u \times \sigma^2 \times p^2 \times u_v^2 \times C^2.$$

The observed bimolecular velocity constant, for a reaction between molecules of the same kind (expressed in gram-molecules per litre per second), is given by:

$$k_{\text{obs.}} = 5.40 \times 10^{31} \cdot u \cdot \sigma^2 \cdot e^{-2E/RT}$$

or

$$k_{\text{obs.}} = 5.40 \times 10^{31} \cdot u \cdot \sigma^2 \cdot p^2 \cdot u_v^2.$$

If the reaction occurs between molecules of different kinds, for example, the union of hydrogen and iodine, the velocity constant is given by:

$$k_{\text{obs.}} = 3.8 \times 10^{31} \cdot \sigma^2 \cdot \sqrt{u_1^2 + u_2^2} \cdot e^{-(E_1 + E_2)/RT}.$$

where u_1 and u_2 are the average velocities of translation of the two kinds of molecules, E_1 is the critical increment of the one kind (per gram-molecule), and E_2 is the corresponding quantity for the other kind. When the bimolecular reaction occurs between nascent atoms, all the reactants are normally in the reactive state, and therefore the exponential term reduces to unity. In such a case, for example, the combination of atoms to form the undissociated molecule of a gas, the bimolecular velocity constant is given by the expression:

$$k = 5.40 \times 10^{21} \cdot u \cdot \sigma^2.$$

(3) The various statements made in (1) and (2) are borne out quantitatively in the cases examined, namely, the decomposition of hydrogen iodide (bimolecular reaction), the union of hydrogen and iodine molecules, and the dissociation of iodine, bromine, chlorine, and hydrogen gases. It is shown that the opposing velocity constants, as well as the equilibrium constants, can be calculated in regions in which, owing to the rate being either extremely great or extremely small, the chemical change cannot be determined experimentally.

(4) The velocity constant of unimolecular decomposition of gaseous hydrogen iodide has been calculated at various temperatures, and is shown to be negligible compared with the bimolecular constant over the range of temperature examined by Bodenstein. In the neighbourhood of 1200° abs., it is calculated that the two velocity constants should be of the same order of magnitude, and therefore the ordinary bimolecular expression should fail to apply quantitatively.

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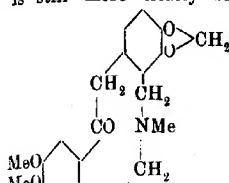
XLII.—*epiBerberine*.

By WILLIAM HENRY PERKIN, jun.

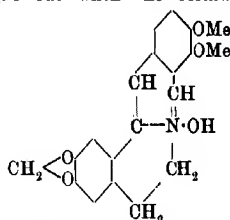
DURING the discussion of the results of an experimental investigation into the constitution of cryptopine, it was pointed out (T., 1916, 109, 833) that the comparison of the formula of this substance with that of berberinium hydroxide* shows that these

* The nomenclature employed in this communication is clearly set out on p. 503.

substances are related in a very striking manner, and this relationship is still more clearly brought out when the formulæ of

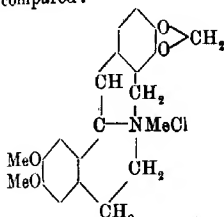
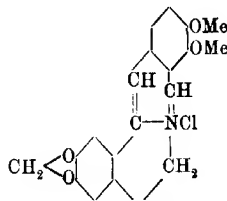


Cryptopine.



Berberinium hydroxide.

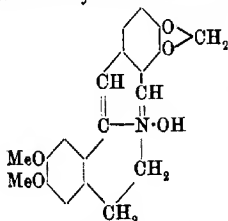
isocryptopine chloride and *berberinium* chloride (*loc. cit.*, p. 833) are compared:


*iso*Cryptopine chloride.


Berberinium chloride.

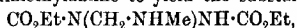
The difference in constitution between the two alkaloids and the two salts is essentially due, first, to the presence of the *N*-methyl group in cryptopine and its absence in the berberine molecule, and, secondly, to the fact that, whereas the four oxygen atoms attached to the two benzene nuclei and carrying the methylene and the two methyl groups, are in the same position in each formula, in the case of cryptopine, the methylenedioxy-group is in the upper and the two methoxy-groups in the lower part of the molecule, whilst in berberinium hydroxide the positions are reversed.

In other words, cryptopine is related to an alkaloid isomeric with ordinary berberinium hydroxide and having the constitution

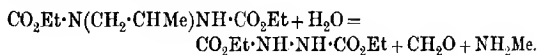

*epi*Berberinium hydroxide.

and it is this substance which has been named *epiberberinum hydroxide*. This substance has, so far, not been met with in nature, and it appeared to the author that it would be an interesting problem to endeavour to prepare it, and thus to be in a position to compare its properties and the properties of its salts with those of berberinum hydroxide and its salts. In order to obtain *epiberberinum* salts from cryptopine, it was essential, in the first place, to discover some method by which the methyl group could be detached from the nitrogen atom in the cryptopine molecule, and this proved to be an undertaking of more than ordinary difficulty.

After several unsuccessful attempts in which various condensing and oxidising agents were employed, the most hopeful course seemed to be the application of a method for removing alkyl groups from nitrogen, which had been discovered by Diels and his pupils (Diels and Fritzsche, *Ber.*, 1911, **44**, 3020; Diels and Paquin, *ibid.*, 1913, **46**, 2000). These investigators have shown that, whereas azodicarboxylic ester, $\text{CO}_2\text{Et}\cdot\text{N}\cdot\text{N}\cdot\text{CO}_2\text{Et}$, combines with primary amines to yield amides, it forms additive compounds with secondary and tertiary amines which are readily hydrolysed by dilute hydrochloric acid, yielding hydrazo-ester together with aldehydes and amines. The important point is that the amines thus formed contain one radicle less than the secondary or tertiary amine employed in the first instance. Thus azodicarboxylic ester combines with dimethylamine to yield the substance,



and this is hydrolysed by dilute hydrochloric acid into hydrazodicarboxylic ester, formaldehyde, and methylamine:



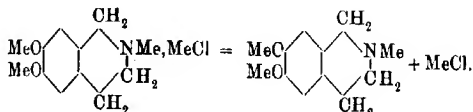
Subsequently, Diels and Ernst Fischer (*Ber.*, 1914, **47**, 2043) showed that *N*-methylpiperidine and complex substances such as atropine, morphine, and codeine could be demethylated by treatment with azodicarboxylic ester followed by hydrolysis with dilute hydrochloric acid.

As there seemed no reason why the same process might not lead to the elimination of the *N*-methyl group in cryptopine, a large number of experiments were made on the action of azodicarboxylic ester on the alkaloid under the conditions recommended by Diels and Fischer in the case of codeine and under various other conditions, including heating the substances together without dilution with a neutral solvent.

In no single case could the formation of an additive product be

observed, and most of the cryptopine was always recovered unchanged when the product of the action was boiled with dilute hydrochloric acid. It is not improbable that this negative result is due, in part at least, to the fact that cryptopine, unlike the alkaloids employed by Diels and Fischer, is very sparingly soluble in boiling acetone and other suitable solvents and also in azodicarboxylic ester, and thus intimate contact with the latter cannot be brought about.

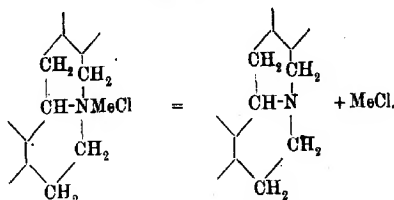
During these experiments, it was noticed that many methochlorides decompose, often at their melting points, with the evolution of gas and formation of a froth, and it was the inquiry into the meaning of this decomposition which ultimately led to the discovery of a process for preparing derivatives of *epiberberine*. One of the first substances to be investigated was 6:7-dimethoxy-2-methyltetrahydroisoquinoline methochloride (see below), because it happened to be available. This substance (1 gram) was placed in a test-tube, the upper part of which was drawn out to a long capillary, and the tube heated in a sulphuric acid bath, when decomposition occurred at about 270°, and, on applying a light to the end of the capillary, the issuing gas burnt with a green-edged flame and was at once recognised as methyl chloride. When effervescence had ceased, the residue was distilled under diminished pressure, and passed over as a colourless syrup which solidified to crystals melting at 83°. This substance was 6:7-dimethoxy-2-methyltetrahydroisoquinoline, so that decomposition had taken place according to the scheme:



In order to investigate a case approximating more closely to that of cryptopine, berberine was converted into tetrahydro-anhydroberberine (tetrahydroberberine), and this into tetrahydro-anhydroberberine methochloride (compare Pyman, T., 1913, 103, 823).

The β -modification of this methochloride was heated in a drawn-out test-tube in a sulphuric acid bath exactly as described above, and again yielded methyl chloride and a dark brown syrup, but this change did not take place until the temperature had reached 285–290°. Less decomposition of the product occurred when the process was carried out under 10 mm. pressure. The residual brown mass separated from alcohol in leaflets which melted at

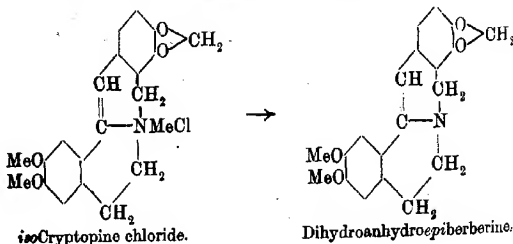
169—171°, and consisted of tetrahydroanhydroberberine, elimination of methyl chloride having occurred according to the partial scheme:



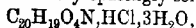
It remained now to apply this method to the quaternary chlorides derived from cryptopine, but, when this was done, great difficulties were at once encountered because of the very high temperatures which are required in order to bring about scission even under diminished pressure.

Indeed, in some of the cases investigated, the temperature necessary to cause elimination of methyl chloride is considerably above the point of decomposition of the product. In such circumstances, the isolation of any of the product is only possible when quite small quantities of material are decomposed at any one time and the experiment is rapidly carried out. The yield, even under the most favourable conditions, is then only a small one, and the preparation of any quantity of material for subsequent examination consequently a very tedious operation.

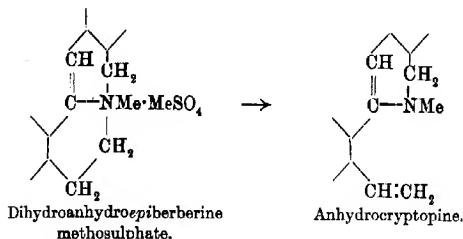
The case most exhaustively studied in the cryptopine series has been that of *isocryptopine* chloride (T., 1916, 109, 883), because this is by far the most accessible of the quaternary chlorides derived from this alkaloid. When *isocryptopine* chloride, in quantities of 1 gram, is heated under diminished pressure, elimination of methyl chloride occurs at about 260°, and it has been found possible to isolate from the black residue, by employing one of the methods described on p. 506, a pure substance which on examination has been found to be *dihydroanhydroepiberberine*:



Dihydroanhydroepiberberine, $C_{20}H_{19}O_4N$, resembles dihydroanhydroberberine* in appearance and in many of its other properties. It melts at $170-172^\circ$, separates from acetone in iridescent, golden plates, and yields a very sparingly soluble hydrochloride,

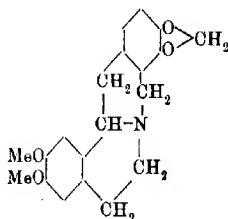


which crystallises in deep yellow, prismatic needles. Dihydroanhydroberberine melts at $170-172^\circ$, separates from acetone in yellow prisms, and is also characterised by the sparing solubility of its hydrochloride, $C_{20}H_{19}O_4N \cdot HCl, 3H_2O$, and other salts which, like the salts of dihydroanhydroepiberberine, are all bright yellow or orange. Dihydroanhydroepiberberine combines with methyl sulphate to yield the methosulphate, $C_{20}H_{19}O_4N \cdot MeSO_4$, which crystallises splendidly in yellow prisms, and when boiled with methyl-alcoholic potassium hydroxide is readily decomposed with



separation of anhydrocryptopine (T., 1916, 109, 975), a decomposition which is a welcome confirmation of the constitution assigned to dihydroanhydroepiberberine.

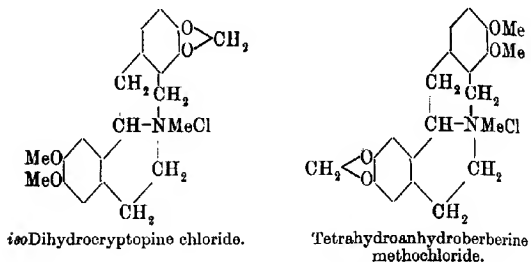
Tetrahydroanhydroepiberberine,



During the course of the investigation of cryptopine, $C_{21}H_{23}O_5N$, it was discovered that this alkaloid is reduced by sodium amalgam with the formation of dihydrocryptopine, $C_{21}H_{25}O_5N$, and this tertiary base, under the influence of acetyl chloride, is converted

* A detailed investigation of this substance is nearly completed, and will, it is hoped, shortly be ready for publication.

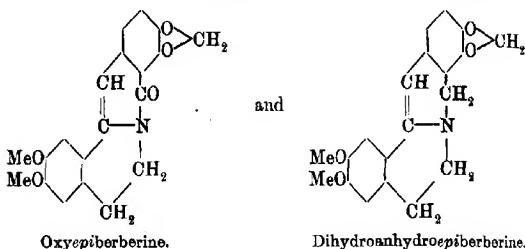
into two stereoisomeric quaternary chlorides, $C_{21}H_{27}O_4NCl$, which were named the α - and β -chlorides of *isodihydrocryptopine* (T., 1916, 109, 839). The close relationship between these chlorides and tetrahydroanhydroberberine methochloride was commented on



at the time, as was also the fact that these substances are the counterpart of one another in all their reactions. It has already been mentioned (p. 495) that tetrahydroanhydroberberine β -methochloride is decomposed on heating with the elimination of methyl chloride and formation of tetrahydroanhydroberberine, and it therefore seemed probable that a similar decomposition would take place in the case of *isodihydrocryptopine chloride* and result in the formation of *tetrahydroanhydroepiberberine*. The first experiments in this direction were disappointing, because the only chloride available was the β -modification, and this does not lose methyl chloride until nearly 300° , and then not readily, with the result that much decomposition of the product occurs. The α -modification of the methochloride is unfortunately very difficult to obtain, since it is produced only in very small quantity during the action of acetyl chloride on dihydrocryptopine. However, a small quantity of the quite pure α -chloride was prepared and found to decompose, when heated under diminished pressure, at a much lower temperature than the β -modification, namely, at about 230° , and the dark-coloured residue could then be purified by the methods given on p. 511, and yields *tetrahydroanhydroepiberberine*. This substance separates from alcohol in colourless needles, and not in the stout prisms so characteristic of tetrahydroanhydroberberine, but in other respects it resembles the latter in a remarkable degree. It melts at the same temperature (170 — 171°) and yields exactly similar, very sparingly soluble salts, of which the hydrochloride, $C_{20}H_{21}O_4N, HCl$, for example, is almost insoluble in dilute hydrochloric acid. It was subsequently found that tetrahydroanhydroepiberberine may be obtained from dihydroanhydroepiberberine by

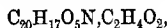
crystals of berberinium chloride, and it is remarkable that the composition of the salt, $C_{20}H_{18}O_4NCl \cdot 4H_2O$, is the same as that of berberinium chloride, and that, on heating, it behaves exactly like the latter and loses $3H_2O$ readily, but the remaining H_2O with much greater difficulty. The *sulphate*, *iodide*, and *nitrate* are also intensely coloured salts, and the picrate melts at 222° , whereas berberine picrate melts at 239 – 240° (Pictet and Gams, *Ber.*, 1911, 44, 2485).

*The Action of Sodium Hydroxide on epiBerberinium Sulphate.
Formation of Oxyepiberberine and Dihydroanhydroepiberberine.*



The remarkable conversion of berberinium sulphate into a mixture of oxyberberine and dihydroanhydroberberine by the action of sodium hydroxide at the temperature of the water-bath was first observed by Gadamer (*Arch. Pharm.*, 1905, 243, 34), and when the same process was applied to *epiberberinium* sulphate, it was found that not only did the reaction proceed in the same direction, but the conversion was even more quantitative than in the case of the berberinium salt. The dihydroanhydro*epiberberine* obtained was compared with the dihydroanhydro*epiberberine* which results from the action of heat on *isocryptopine* chloride (p. 506), and the two preparations were found to be identical.

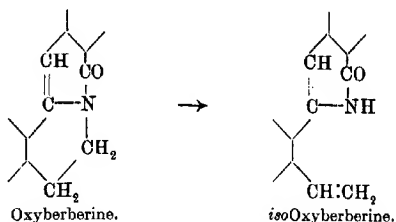
Oxyepiberberine, $C_{20}H_{17}O_5N$, melts at 240 – 241° , and has properties which are very similar to those of oxyberberine (m. p. 198 – 200°). Both are feeble bases and crystallise from acetic acid in the form of their beautifully crystalline acetates,



which are dissociated by water or when they are heated at 80 – 90° into acetic acid and oxy-berberine or -*epiberberine*.

When oxyberberine is heated in a sealed tube with dilute hydrochloric acid at 130° , it gradually undergoes isomeric change and

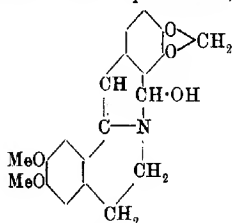
yields *isooxyberberine*, the conversion taking place in the following direction:



(Perkin and Robinson, T., 1912, **101**, 262). This curious process does not take place at 130° in the case of *oxyepiberberine*, but is rapid and quantitative at about 150–160°. *isoOxyepiberberine*, like the corresponding berberine derivative, is practically devoid of basic properties; it does not melt at 300°, and is even more sparingly soluble in the usual solvents than *isooxyberberine* (m. p. 245°), but it may be recrystallised from pyridine.

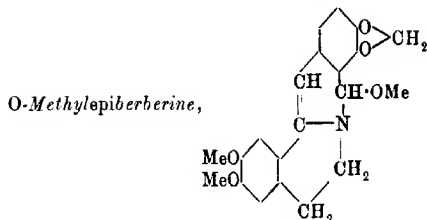
The alkaloid, berberine, $C_{20}H_{19}O_5N$, was first isolated by Gadamer (*Arch. Pharm.*, 1905, **243**, 33), who obtained it by adding a large excess of sodium hydroxide to berberinium hydroxide (or the sulphate) and extracting with ether. It crystallises from ether in yellow needles and melts at 144°.

During the course of this investigation, experiments on the action of sodium hydroxide on *epiberberine* sulphate were made under the conditions recommended by Gadamer in the hope that it might prove possible to isolate *epiberberine*,



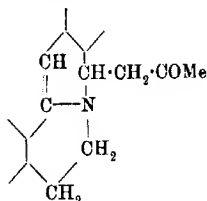
These were, however, only partly successful, since the *epiberberine*, which was obviously formed, could not be isolated in a pure condition.

The substance always contained *oxyepiberberine*, which seems to be produced as the result of oxidation even when the ethereal solution of *epiberberine* remains in contact with air. On the other hand, the *O*-methyl and *O*-ethyl derivatives have been obtained in a pure condition.



and O-Ethylepiberberine.

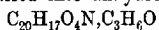
G. M. and R. Robinson (T., 1917, 111, 967) have recently shown that berberine is converted by treatment with methyl alcohol in the cold into *O*-methylberberine (methoxydihydroberberine), and the corresponding ethyl derivative is obtained when ethyl alcohol is employed. The present author finds that these substances are more conveniently prepared by the action of sodium methoxide or ethoxide on berberinium sulphate, and hopes shortly to publish the details of these and other experiments on several new derivatives of berberine. *O*-Methyl and *O*-ethyl derivatives of epiberberine are obtained under exactly similar conditions. Thus epiberberinium chloride (or the sulphate) yields, on treatment in methyl-alcoholic suspension with sodium methoxide, *O*-methylepiberberine, $\text{C}_{20}\text{H}_{18}\text{O}_4(\text{OMe})\text{N}$, which separates from methylal in splendid brownish-yellow prisms and melts at $150\text{--}152^\circ$. The corresponding *O*-ethyl derivative does not crystallise so readily and melts at $135\text{--}136^\circ$. Both these substances dissolve in boiling dilute hydrochloric acid, and, on cooling, epiberberinium chloride separates. They also dissolve readily in boiling acetone, and when the solution is concentrated and set aside, anhydroepiberberine-acetone, $\text{C}_{20}\text{H}_{17}\text{O}_4\text{N}_3\text{C}_3\text{H}_6\text{O}$, separates. This interesting substance, which doubtless contains the grouping



melts at 162° , crystallises in yellow prisms, and is, in appearance and properties, exactly analogous to anhydroberberine-acetone (m. p. 175°), which is similarly produced when *O*-methyl- or *O*-ethyl-berberine is dissolved in boiling acetone.

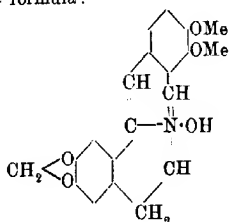
The Nomenclature of Berberine and its Salts.

During the last few years, some difficult points connected with the constitution of berberine and its salts, which still remained, have been definitely cleared up, and it seems to the author that a system of nomenclature should now be adopted which is in accordance with the new views. There can be no doubt that the alkaloid exists in two distinct modifications, one of which is crystalline and the other so far known only in solution. When a solution of the sulphate is mixed with the quantity of barium hydroxide necessary for the removal of the sulphuric acid, the filtered solution is strongly alkaline, and a similar alkaline solution is obtained when superheated steam is passed into anhydroberberine-acetone,

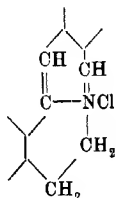


(Gadamer, *Arch. Pharm.*, 1905, **243**, 33).

Unfortunately, it has not been found possible to isolate this soluble alkaline modification of the alkaloid, since decomposition occurs during evaporation even at the ordinary temperature in a vacuum desiccator, but it is now generally recognised that this alkaline solution contains the ammonium hydroxide modification represented by the formula:



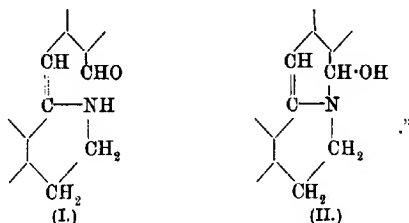
It is clear that this modification, from which the salts are obtained by the replacement of the hydroxyl group by acid radicles, may conveniently and correctly be termed *berberinium hydroxide*. The salt commonly known as berberine hydrochloride is, of course, not a hydrochloride, but a quaternary chloride containing the grouping



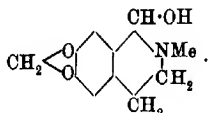
and must therefore be named *berberinium chloride*.

The solid modification of the alkaloid was first isolated by Gadamer (*loc. cit.*, p. 33), who obtained it by adding a large excess of sodium hydroxide to the aqueous solution of berberinium hydroxide, or the sulphate, and extracting with ether. It crystallises from ether in yellow needles, melts at 144° , and has the composition $C_{20}H_{19}O_5N$.

Owing to the fact that this modification yielded oxyberberine and dihydroberberine on treatment with hot concentrated sodium hydroxide solution, and therefore behaved like an aromatic aldehyde, Gadamer considered that the substance was an aldehyde of the formula I, and he therefore named it "berberinal." On the other hand, Tinkler (T., 1911, **99**, 1345) was led to the conclusion that "the evidence obtained from the spectroscopic examination of berberinal points to the fact that the substance is not the aldehyde (I), but the carbinol modification (II) of the alkaloid:



In a paper, published in 1912, on the exhaustive methylation of tetrahydroanhydroberberine (McDavid, Perkin, and Robinson, T., **101**, 1219), the carbinol formula for the alkaloid was accepted, and recently (T., 1917, **111**, 958) G. M. and R. Robinson adopted the same view, mainly as the result of a comparison of the behaviour of berberinal and cotarnine,

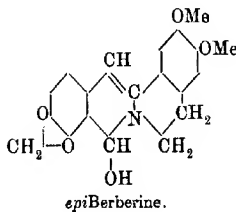
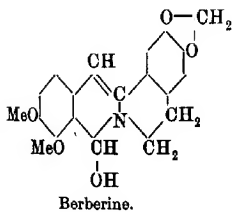


towards acetone, alcohols, amides, and other substances, with which both bases yield similarly constituted and highly characteristic condensation products. Since berberinal is obtained by the action of alkali on the salts of berberine, and on the other hand is converted into the salts of berberine by solution in acids, it appears to the author that it should, in future, be called "berberine," a plan which would do away with the anomaly

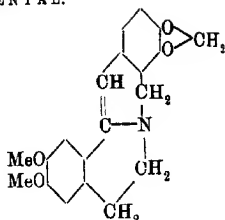
that, whereas the salts of berberine are recognised, there is, at the present time, no berberine corresponding with them. The quaternary salts of berberine, which are derived from berberinium hydroxide, should, then, be called "berberinium salts," so, for example, berberinium chloride, $C_{20}H_{18}O_4NCl$, nitrate, $C_{20}H_{18}O_4N,NO_3$, etc. The adoption of this system of nomenclature necessitates a change in the names of the reduction products derived from berberine. The substances called dihydroberberine, $C_{20}H_{19}O_4N$, and tetrahydroberberine, $C_{20}H_{21}O_4N$, are not direct reduction products of berberine, $C_{20}H_{18}O_5N$, but are derived from the alkaloid by reduction and simultaneous removal of the elements of water. Their names must therefore be altered to *dihydroanhydroberberine* and *tetrahydroanhydroberberine* respectively. Acetoneberberine, $C_{20}H_{18}(CH_2 \cdot COMe)O_4N$, is formed from berberine by condensation with acetone, with the elimination of water, and should therefore be named anhydroberberineacetone, when its relationship to anhydrocotarnineacetone is at once recognised.

It is clear that the similar condensation products of berberine with 2-methylindole, acetophenone, cyclohexanone, etc. (compare G. M. and R. Robinson, T., 1917, 111, 959), are also anhydroberberine derivatives.

It may be pointed out that the actual placing of the berberine formulæ in the present communication has been employed in order to bring out clearly the similarity in constitution between cryptopine and berberine or *epiberberine*, but, for most purposes, there is much to be said in favour of writing the formulæ for berberine and *epiberberine* in the following manner:



EXPERIMENTAL.

Dihydroanhydroepiberberine,

This substance is obtained, as explained on p. 496, when *isocryptopine* chloride is heated, and it is important that the chloride employed should be quite free from *cryptopine* hydrochloride, that is, that it should give no precipitate when its aqueous solution is made alkaline with ammonia and boiled.* If any *cryptopine* hydrochloride is present, much decomposition occurs during the heating, and the product is, of course, contaminated with *cryptopine*, and consequently difficult to purify.

The finely powdered and sieved chloride, after being carefully dried in the steam-oven, is placed, in quantities of not more than 2 grams, in a wide test-tube fitted with a cork and bent tube, the whole connected with a good water pump, and exhausted to, at the most, 15 mm. The test-tube, placed in a metal-bath, is gradually heated until any moisture has been removed, the temperature is then raised, rather rapidly, to 220°, during which the powder darkens in colour, and is apt to be projected about the test-tube and into the bent delivery tube.

Decomposition soon sets in, with frothing and formation of a dark brown, viscous mass, and, so soon as the disengagement of methyl chloride becomes rapid, the temperature is allowed to drop to 200—205°, and kept at this for three or four minutes and until the frothing has almost subsided. In order that the operation may be successful, the decomposition must be carried out as rapidly as possible, and the experiment requires considerable practice. The hot tube is allowed to cool slightly and then plunged into

* *isocryptopine* chloride, prepared by the action of phosphoryl chloride on *cryptopine* (T. 1916, 109, 883) frequently contains traces of *cryptopine* hydrochloride. When this is the case, the whole is dissolved in boiling water, the solution made alkaline with ammonia, heated on the water-bath for some minutes and then filtered from the trace of *cryptopine*. The filtrate, on keeping, deposits a voluminous precipitate of pure *isocryptopine* chloride. This quaternary salt dissolves moderately readily in boiling glacial acetic acid, and separates well as a voluminous mass of colourless groups of needles, a method which yields the salt in an exceptionally pure state.

water so that the resin may crack, become detached from the sides of the tube, and easily rubbed off with a glass rod; otherwise, if the tube is allowed to cool slowly, the resin becomes very firmly attached and is most difficult to scrape off. The crude, dark brown product may then be treated in two different ways in order to extract the dihydroanhydroepiberberine.

(1) The resin is dissolved in hot dilute acetic acid (25 per cent.), the dark brown solution precipitated with ammonia, the gelatinous precipitate immediately extracted with much ether, and the ethereal solution decanted or rapidly filtered from the troublesome limy precipitate, which consists largely of unchanged *isocryptopine* chloride. After drying over potassium carbonate, filtering, and concentrating, the ethereal solution is left in the ice-chest, when it gradually deposits a brick-red, crystalline precipitate which, after collecting and washing with ether, consists of almost pure dihydroanhydroepiberberine. This substance may be obtained quite pure by repeating the solution in dilute acetic acid, precipitation with ammonia, and extraction with ether, or it may be recrystallised from methyl alcohol or acetone (see below).

(2) The finely powdered resin is boiled with water, which extracts unchanged *isocryptopine* chloride and a dark reddish-brown impurity, the precipitate is collected by the aid of the pump, and washed with hot water until the filtrate is no longer red. The residue, after draining on porous porcelain, is triturated with methyl alcohol in a mortar, filtered, and the precipitate washed with methyl alcohol until the filtrate is only yellow. The ochreous residue of nearly pure dihydroanhydroepiberberine melts at $165-168^{\circ}$, and was employed in this condition for many of the experiments described in the following pages.* For analysis, the substance was recrystallised from acetone, and two analyses were made with preparations obtained by the two processes described above.

(1) 0.1072 gave 0.2793 CO_2 and 0.0564 H_2O . $\text{C}=71.1$; $\text{H}=5.8$.
0.3967 „ 14.1 c.c. N_2 at 16° and 762 mm. $\text{N}=4.2$.

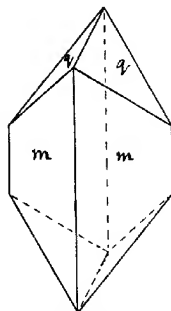
* Owing to the tedious nature of these processes and the labour required in the preparation even of a few grams of dihydroanhydroepiberberine, attempts have repeatedly been made to discover conditions under which larger quantities than 2 grams of *isocryptopine* chloride could be decomposed in one operation, but without success. If, for example, 10 grams of the chloride are heated in a small flask under exactly the conditions observed in the case of the 2 grams, the decomposition appears to proceed in precisely the same way, but the product yields, at the most, traces only of pure dihydroanhydroepiberberine. Apparently the time required to decompose 10 grams of *isocryptopine* chloride is sufficiently long to decompose the product almost entirely.

(2) 0.1179 gave 0.3075 CO_2 and 0.0615 H_2O . $\text{C}=71.1$; $\text{H}=5.7$. $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}$ requires $\text{C}=71.2$; $\text{H}=5.6$; $\text{N}=4.2$ per cent.

Dihydroanhydroepiberberine melts at $172\text{--}174^\circ$, and is sparingly soluble in ether or in ethyl or methyl alcohol, even on boiling, and also in cold acetone. It is moderately soluble in boiling acetone, and separates in magnificent iridescent, golden-yellow plates resembling lead iodide, or, if the solution is allowed to cool slowly, in well-defined prisms.

The crystals, obtained from acetone, were measured by Miss M. W. Porter, and the Fedorov complex-symbol was calculated by Mr. T. V. Barker.

The crystals are monoclinic with axial ratios: $a:b:c=1.163:1.0:0.995$; $\beta=97^\circ 15'$. Determinations: 100/001/010. Complex-



Dihydroanhydroepiberberine.

symbol, $4o$; $8/44/+4$. The forms observed were $m\{110\}$ and $q\{011\}$, with a prismatic habit as shown in the figure. The faces being rounded, the reflections were rather poor. Four crystals were measured and the results obtained are placed in the following table.

Face.	No. of readings.	Azimuth (ϕ).			Polar distance (ρ).		
		Limits.	Obs	Calc	Limits	Obs.	Calc
$m\{110\}$	11	$40^\circ 39' - 41^\circ 13'$	$*40^\circ 56'$	—	$90^\circ 0' - 90^\circ 9'$	$90^\circ 0'$	$90^\circ 0'$
$q\{011\}$	4	$6^\circ 42' - 7^\circ 52'$	$*7^\circ 7'$	—	$44^\circ 56' - 45^\circ 15'$	$*45^\circ 5'$	—

Dihydroanhydroepiberberine dissolves readily in acetic acid to a deep yellow solution, and the base is not precipitated by dilution with water, but separates on the addition of ammonia as a caseous precipitate which, on warming, becomes crystalline. If a trace of the base, dissolved in a drop of acetic acid, is mixed with sulphuric

acid, there is at first little change, but, on keeping, the solution becomes cherry-red.

Salts of Dihydroanhydroepiberberine.

Hydrochloride, $C_{20}H_{19}O_4N.HCl.3H_2O$.—When dihydroanhydroepiberberine is moistened with hydrochloric acid, it is converted into a yellow powder of the hydrochloride which, whilst very sparingly soluble in cold water, and particularly so in cold dilute hydrochloric acid, dissolves in much boiling water and separates in groups of flat, yellow, prismatic needles. This brilliant orange salt loses its water of crystallisation and becomes brick-red in the steam-oven, but on exposure to the air, it gradually absorbs moisture and becomes yellow again:

0.1319, air-dried salt, lost 0.0157 at 100° . $H_2O=11.9$.
0.1048, dried at 100° , gave 0.2470 CO_2 and 0.0490 H_2O .
 $C=64.2$; $H=5.2$.

$C_{20}H_{19}O_4N.HCl.3H_2O$ requires $H_2O=12.6$ per cent., and the anhydrous salt requires $C=64.2$; $H=5.3$ per cent.

Hydrobromide.—The addition of boiling dilute potassium permanganate to the boiling solution of the hydrochloride gives a brick-red precipitate which consists of groups of striated prismatic needles. For analysis, it was dried at 100° :

0.0810 gave 0.1705 CO_2 and 0.0343 H_2O . $C=57.4$; $H=4.7$.

$C_{20}H_{19}O_4N.HBr$ requires $C=57.4$, $H=4.8$ per cent.

Dihydroanhydroepiberberine Methosulphate, $C_{20}H_{19}O_4N.Me_2SO_4$.—This derivative is best prepared by sealing up the finely divided base (1 gram) with freshly distilled methyl sulphate (1.5 c.c.) in a small tube and shaking vigorously from time to time. There is no evolution of heat on mixing, and combination takes place only very gradually, but is complete in about eight days. The product is triturated with benzene, the yellow mass collected by the aid of the pump, washed with benzene, and recrystallised from methyl alcohol, in which it is sparingly soluble. The prisms which separate on gradual cooling are unfortunately so striated as to be unsuitable for measurement, and the substance also becomes opaque when exposed to the air.

After remaining exposed to the air for eight days, the substance lost only 3.1 per cent. at 100° , and on analysis:

0.1013 gave 0.2115 CO_2 and 0.0531 H_2O . $C=56.9$; $H=5.8$.

$C_{20}H_{19}O_4N.Me_2SO_4$ requires $C=57.0$; $H=5.4$ per cent.

Dihydroanhydroepiberberine methosulphate darkens above 250°

and melts rather sharply at 260° with vigorous decomposition to a black froth. The deep yellow prisms from methyl alcohol become pale yellow on stirring with water, dissolve very sparingly in the cold, but much more freely on boiling, and the solution gelatinises if rapidly cooled. The aqueous solution gives no precipitate with ammonia, and rapidly reduces permanganate even at -5° .

This methosulphate is sparingly soluble in glacial acetic acid, and the addition of sulphuric acid produces, at first, no coloration, then a pale green gradually develops; on keeping, the solution becomes purplish-black, and the addition of a drop of dilute nitric acid changes the colour to intense purple and then to brown. When the finely divided methosulphate is mixed with methyl-alcoholic potassium hydroxide (15 per cent.), it dissolves, but, on boiling, the solution clouds and a pale yellow precipitate separates. This was collected, washed with methyl alcohol, then with water, and dissolved in boiling methyl alcohol, when, on rubbing, minute yellow prisms immediately separated which melted at $108-110^{\circ}$, and consisted of anhydrocryptopine (p. 497).

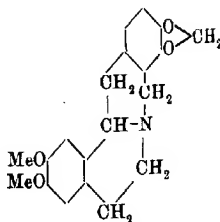
Dihydroanhydroepiberberine methiodide, $C_{20}H_{19}O_4N, MeI$, is obtained as an immediate, very sparingly soluble, ochreous precipitate when potassium iodide is added to the saturated aqueous solution of the methosulphate, but if the solutions are sufficiently dilute and are mixed boiling, a clear solution may be obtained, from which the iodide separates as a fluffy precipitate consisting of microscopic groups of needles:

0.1135 gave 0.2176 CO_2 and 0.0487 H_2O . $C=52.3$; $H=4.7$.

$C_{20}H_{19}O_4N, MeI$ requires $C=52.6$; $H=4.6$ per cent.

This methiodide darkens and softens at about 230° , and then melts and decomposes at about 245° to a deep red syrup.

Tetrahydroanhydroepiberberine,



This substance is most readily obtained by the action of heat on *isodihydrocryptopine* α -chloride (T., 1916, 109, 935), but it may also be prepared by the action of heat on the corresponding β -chloride (*loc. cit.*, p. 934). In the case of the α -chloride, the

decomposition is conveniently carried out by heating quantities of not more than 2 grams of the pure dry salt in a test-tube, drawn out to a long capillary, by means of a sulphuric acid bath. At about 270° effervescence sets in, due to the escape of methyl chloride, which may be ignited at the end of the capillary and burns with a green-edged flame.

As soon as the frothing has ceased, the tube is taken out of the bath and left to cool, when the brown syrup will have solidified and the dark product may be purified by crystallisation from boiling alcohol, from which nearly pure tetrahydroanhydroepiberberine separates at once in pale brown needles. An alternative method is to convert the crude product into the very sparingly soluble hydrochloride (see below), to purify this by crystallisation from acetic acid, and, after decomposing the colourless salt with dilute alkali, to crystallise the base from much alcohol.

In the case of the β -chloride, decomposition does not proceed so smoothly, owing no doubt to the fact that this chloride fuses with much greater difficulty than the α -chloride. The elimination of methyl chloride is best carried out with quantities of not more than 2 grams in a test-tube heated in a metal-bath under the conditions described in detail in the case of the preparation of dihydroanhydroepiberberine from isocryptopine chloride (p. 506). The decomposition of the β -chloride does not begin much below 300°, and should not be pushed to completion, otherwise the product will be very dark coloured and difficult to purify. Purification is best effected by converting the dark resin into the sparingly soluble hydrochloride, crystallising this from acetic acid until it is quite colourless, and then regenerating the base and crystallising this from much alcohol.

Preparation of Tetrahydroanhydroepiberberine by the Reduction of Dihydroanhydroepiberberine.—In the event of the α - or β -chlorides of isodihydrocryptopine not being available, this method is probably the most convenient for the preparation of the tetrahydro-base. Crude dihydroanhydroepiberberine (p. 507) is dissolved in hot concentrated hydrochloric acid, the solution diluted with an equal volume of water, and boiled with a large excess of granulated tin for several hours. The product, diluted with much water, is freed from tin by means of hydrogen sulphide in the usual manner, the filtrate from the tin sulphide is concentrated and left for several days, during which the sparingly soluble hydrochloride of tetrahydroanhydroepiberberine separates. This is collected, recrystallised, decomposed by alkali, and the base crystallised from much alcohol. Two different specimens gave the following results on analysis:

0.1015 gave 0.2625 CO_2 and 0.0569 H_2O . $\text{C}=70.5$; $\text{H}=6.2$.
 0.1021 „ 0.2652 CO_2 „ 0.0575 H_2O . $\text{C}=70.8$; $\text{H}=6.3$.
 0.3965 „ 14.1 c.c. N_2 at 15° and 758 mm. $\text{N}=4.2$.

$\text{C}_{20}\text{H}_{21}\text{O}_4\text{N}$ requires $\text{C}=70.8$; $\text{H}=6.2$; $\text{N}=4.2$ per cent.

Tetrahydroanhydroepiberberine melts at $170\text{--}171^\circ$ and is sparingly soluble in boiling methyl alcohol, but somewhat more readily so in boiling ethyl alcohol, from both of which it separates in colourless needles. It is sparingly soluble in cold acetone, moderately readily so on boiling, and crystallises on slowly cooling in prisms; boiling benzene dissolves the base freely, and, on cooling, it separates in prismatic needles. In purifying specimens of the base, which are highly coloured, acetone is the best solvent. *Tetrahydroanhydroepiberberine* does not exhibit the tendency so marked in the case of *tetrahydroanhydroberberine* of separating from solvents in stout, well-developed prisms, and unfortunately all attempts to obtain it in a state suitable for measurement have so far been unsuccessful. The solution of a crystal in a drop of acetic acid gives at first no coloration on the addition of sulphuric acid, but gradually a violent tint develops.

Salts of Tetrahydroanhydroepiberberine.

Hydrochloride, $\text{C}_{20}\text{H}_{21}\text{O}_4\text{N}, \text{HCl}$.—The finely powdered base is immediately converted by moistening with dilute hydrochloric acid into the sparingly soluble hydrochloride, which separates from much boiling water in microscopic bundles of needles like fern fronds:

0.1140 gave 0.2687 CO_2 and 0.0608 H_2O . $\text{C}=64.3$; $\text{H}=5.9$.

$\text{C}_{20}\text{H}_{21}\text{O}_4\text{N}, \text{HCl}$ requires $\text{C}=64.0$; $\text{H}=5.8$ per cent.

In its properties, this hydrochloride resembles the sparingly soluble hydrochloride of *tetrahydroanhydroberberine*, but it appears to be even less readily soluble than the latter in dilute hydrochloric acid, and must be classed as one of the least readily soluble of alkaloid hydrochlorides. When it is heated in a capillary tube, the upper surface in contact with air begins to darken at $195\text{--}200^\circ$, and becomes orange-red, whilst the remainder is scarcely discoloured; at $285\text{--}290^\circ$, the whole melts with vigorous effervescence to an orange-red froth. Highly coloured specimens of the hydrochloride are readily obtained colourless by recrystallisation from glacial acetic acid, in which the salt is sparingly soluble and from which it separates in colourless nodules or circular, warty groups, the colouring matter remaining almost entirely in the mother liquor.

The *sulphate* is much more readily soluble than the hydrochloride, and separates either as a jelly or as a voluminous mass of bent and striated needles. When the aqueous solution of this salt is boiled, a very sparingly soluble sulphate gradually separates as a sandy powder.

The *nitrate* separates, on the addition of dilute nitric acid, to the hot solution of the sulphate, as a very sparingly soluble, crystalline powder.

Tetrahydroanhydroepiberberine Methosulphate and its Conversion into Anhydrodihydrocryptopine (A and B).—When tetrahydroanhydroepiberberine (3 grams) is mixed with freshly distilled methyl sulphate (4 c.c.), the mixture becomes very warm, liquefies, and then sets to a stiff paste of the methosulphate, which may be freed from the excess of methyl sulphate by washing with benzene and then be crystallised from methyl alcohol. A more convenient method of preparation is to dissolve the base (2 grams) in boiling benzene (10 c.c.), and, after cooling until crystallisation just commences, to add freshly distilled methyl sulphate (3 c.c.).

The clear solution soon begins to deposit the methosulphate as a hard crust, which is collected, washed with benzene, and crystallised from methyl alcohol. An air-dried specimen of the needle-shaped modification of the substance which separates from water (see below) appears to have the formula $C_{20}H_{21}O_4N, Me_2SO_4, 3H_2O$:

0.7220, air-dried salt, lost 0.0834 at 100° . $H_2O = 11.5$.

0.1201, dried at 100° , gave 0.2486 CO_2 and 0.0635 H_2O . $C = 56.5$; $H = 5.9$.

$C_{20}H_{21}O_4N, Me_2SO_4, 3H_2O$ requires $H_2O = 10.4$ per cent., and the anhydrous substance requires $C = 56.7$, $H = 5.9$ per cent.

Tetrahydroanhydroepiberberine methosulphate melts and decomposes at about $255-260^\circ$; it is sparingly soluble in cold methyl alcohol, but readily so on boiling, and separates in large, colourless prisms. It is sparingly soluble in cold water, but dissolves readily on boiling, and the solution either sets to a jelly or deposits the substance in groups of hairs. At some concentrations, the methosulphate is deposited in groups of striated prisms; the liquid then becomes filled with glistening needles, and when warmed the needles dissolve and the prisms remain. It is therefore probably dimorphous.

The hot dilute aqueous solution of the methosulphate gives, on the addition of boiling dilute potassium iodide, a clear solution, from which the iodide separates as a voluminous mass of fine hairs. This substance is isodihydrocryptopine α -iodide, since it melts at

275° and behaves on heating exactly as described in the case of that substance (compare T., 1916, **109**, 937).

Anhydrodihydrocryptopine (A and B).—When tetrahydroanhydroepiberberine methosulphate was heated with excess of methyl-alcoholic potassium hydroxide (25 per cent.), it dissolved; the solution then became lilac, and decomposition soon set in, with the separation of potassium sulphate.

After twenty minutes, water was added, the viscid precipitate, which soon became crystalline, collected, left on porous porcelain until dry, and crystallised from much methyl alcohol, in which it was very sparingly soluble. The glistening mass of microscopic prisms which separated on keeping melted at 177—178°, and consisted of anhydrodihydrocryptopine (A), since, on boiling with alcohol for half an hour, evaporating to dryness, and crystallising from methyl alcohol, prisms of anhydrodihydrocryptopine (B) melting at 127° separated (T., 1916, **109**, 941). On analysis, the modification melting at 177—178° gave C=71.1, H=6.8, whereas $C_{21}H_{23}O_4N$ requires C=71.4; H=6.5 per cent.

The epiBerberinium Quaternary Salts (compare p. 499).

These salts are obtained from the salts of dihydroanhydroepiberberine or tetrahydroanhydroepiberberine by the action of such oxidising agents as bromine, iodine, dilute nitric acid, or mercuric acetate, and of these, the latter reagent, first recommended by Gadamer (*Arch. Pharm.*, 1915, **253**, 274) for such oxidations, gives the best results.

(1) *The Action of Iodine on Tetrahydroanhydroepiberberine.*—

In studying this process, the pure base (8 grams) was dissolved in boiling alcohol, and then an alcoholic solution of rather less than the calculated quantity of iodine (11 instead of 12 grams) was added in small quantities at a time. The colour disappeared rapidly, especially at first, and a heavy, crystalline precipitate soon commenced to separate. After boiling for thirty minutes, most of the alcohol was distilled off, the residue mixed with very dilute sulphurous acid to remove a trace of iodine, the ochreous precipitate collected, washed, and then boiled for an hour with water and excess of freshly precipitated silver chloride. The product was filtered, the filtrate and washings being concentrated considerably, made slightly alkaline with ammonia, and left in the ice-chest for a couple of days. The brown liquid was filtered from a small quantity of a crystalline base which had separated, the filtrate heated to boiling, and mixed with a large excess of hydrochloric acid. After remaining over night, the crystalline salt was collected

and several times recrystallised from dilute hydrochloric acid, when pure *epiberberinium* chloride was obtained in deep orange needles. For analysis, the salt was dried in the steam-oven at about 90°:

0.1002 gave 0.2265 CO₂ and 0.0476 H₂O. C=61.7; H=5.2.

C₂₀H₁₈O₄NCl.H₂O requires C=61.6; H=5.2 per cent.

(2) *The Action of Mercuric Acetate on Tetrahydroanhydroepiberberine.*—This process was the one employed in the preparation of much of the *epiberberinium* chloride required for this research. Tetrahydroanhydro*epiberberine* (3.5 grams), dissolved in dilute acetic acid (40 c.c. of 25 per cent.), was heated to 50°, and then a solution of mercuric acetate (prepared by dissolving 9 grams of mercuric oxide in hot glacial acetic acid and adding 3 vols. of hot water) was slowly added, when oxidation took place at once and mercurous acetate separated. After heating for a few minutes on the steam-bath, the whole was left in the ice-chest over night, in order that as much mercurous acetate as possible should crystallise out, then filtered by the aid of the pump, and the precipitate washed with ice-water. Hydrogen sulphide was then passed until the liquid smelled strongly of the gas, the whole was then heated on the water-bath, filtered from the mercuric sulphide,* the filtrate made alkaline with ammonia, and left for two days.

A small quantity of unchanged tetrahydroanhydro*epiberberine* which had separated was removed by filtration, the brown filtrate made just acid with hydrochloric acid, concentrated by distillation under diminished pressure, and mixed with a large excess of hydrochloric acid. Almost immediately, *epiberberinium* chloride commenced to separate in orange needles, and this was collected, left in contact with porous porcelain until dry, and washed with a little methyl alcohol, which removed a dark-coloured impurity. Finally, the salt was crystallised from dilute hydrochloric acid, from which it separated in orange needles possessing a striking, satiny lustre. Analysis (1) given below was made with a sample prepared by this process.

(3) *The Action of Mercuric Acetate on Dihydroanhydroepiberberine.*—This process, which works well, is conveniently carried out by dissolving dihydroanhydro*epiberberine* (3.5 grams) in dilute

* It is necessary to remove any trace of mercuric salt before precipitating the *epiberberinium* chloride with hydrochloric acid, because otherwise the latter will be contaminated with mercuric double salt. On the other hand, if the solution of the *berberinium* acetate, as sometimes happens, is very dark coloured, it is a good plan to add excess of mercuric chloride and hydrochloric acid and then to collect the mercuric double salt and decompose this with hot water and hydrogen sulphide. The filtrate is then much less coloured, and yields, on concentration, very pure *epiberberinium* chloride.

acetic acid (30 c.c. of 25 per cent.), adding a solution of mercuric acetate prepared from 4.5 grams of mercuric oxide, and, after remaining over night, heating on the steam-bath for half an hour. The product is worked up exactly in the way explained in detail in the case of the corresponding oxidation of tetrahydroanhydro-*epiberberine* (see above), and yields about 2 grams of pure *epiberberinium chloride* (see analysis 2).

epiBerberinium chloride, $C_{20}H_{18}O_4NCl \cdot 4H_2O$, separates from water, in which it is comparatively readily soluble, in brilliant orange needles, which when dry have a striking, satiny lustre. It is much less readily soluble in dilute hydrochloric acid than in water, and is best crystallised by adding concentrated hydrochloric acid to the moderately concentrated aqueous solution. It is very sparingly soluble in boiling methyl alcohol, but separates beautifully in striated, orange needles; on the other hand, it dissolves readily in hot glacial acetic acid, and crystallises well from this solvent. When the glistening, orange needles of the chloride are moistened with methyl alcohol, they lose their lustre and become an opaque chrome-yellow powder, a change doubtless due to the loss of the water of crystallisation:

(1) 0.1136, air-dried salt, lost 0.0139 in the steam-bath at about 90° . $H_2O = 12.2$.

0.0997 then gave 0.2273 CO_2 and 0.0472 H_2O . $C = 62.1$; $H = 5.2$.

(2) 0.1073 dried at about 90° gave 0.2437 CO_2 and 0.0491 H_2O . $C = 61.9$; $H = 5.1$.

$C_{20}H_{18}O_4NCl \cdot 4H_2O$ losing $3H_2O = 12.17$ per cent.

$C_{20}H_{18}O_4NCl \cdot H_2O$ requires $C = 61.6$; $H = 5.1$ per cent.

In an experiment in which the salt had been heated in an air-bath at $100-105^\circ$, it had darkened somewhat and gave $C = 63.7$, $H = 4.8$, whereas $C_{20}H_{18}O_4NCl$ requires $C = 64.6$, $H = 4.8$ per cent. The salt was therefore practically anhydrous.

The *platinichloride* separates as a bright orange-red precipitate when platinic chloride is added to the warm solution of *epiberberinium chloride* in dilute hydrochloric acid:

0.1148 gave 0.1878 CO_2 and 0.0351 H_2O . $C = 44.6$; $H = 3.4$.

$(C_{20}H_{18}O_4NCl)_2PtCl_4$ requires $C = 44.4$; $H = 3.3$ per cent.

epiBerberinium sulphate is obtained when hot dilute sulphuric acid is added to a concentrated solution of the chloride as a bright yellow salt which crystallises in needles.

The characteristic *picrate* separates as an orange, amorphous precipitate when picric acid is added to a hot dilute solution of the chloride. It melts not very sharply at 222° with decomposition, and is very sparingly soluble even in much boiling water. It is also

very sparingly soluble in boiling alcohol, in which it dissolves to the extent of about 1 gram in a litre, and, on cooling, separates almost completely in flat, microscopic needles melting at 222° .

Action of Sodium Hydroxide on epiBerberinium Sulphate.

Formation of epiBerberine (epiBerberinal), Oxyepiberberine, and Dihydroanhydroepiberberine (compare p. 500).

In the introduction to this communication (p. 501), it is explained that berberine (berberinal) is readily obtained by treating berberinium sulphate with concentrated aqueous sodium hydroxide and extracting with ether (Gadamer, *Arch. Pharm.*, 1905, **243**, 34), but this process has not been found so successful in the case of epiberberinium sulphate. The best result is obtained when an excess of sodium hydroxide (50 per cent.) is added to a solution of epiberberinium sulphate (5 grams) in 500 c.c. of freshly boiled water. The ochreous precipitate which separates is rather sparingly soluble in ether, and the filtered ethereal solution begins almost immediately to deposit needles of oxyepiberberine (see below). If, however, the ochreous precipitate is immediately collected in an atmosphere of coal gas, it is almost completely soluble in dilute hydrochloric acid with the formation of epiberberinium chloride, and yields, on analysis, numbers agreeing approximately with those required for the formula of epiberberine:

0.1090 gave 0.2693 CO_2 and 0.0540 H_2O . $\text{C}=67.4$; $\text{H}=5.4$.

$\text{C}_{20}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{C}=68.0$; $\text{H}=5.4$ per cent.

Oxidation takes place rapidly when the moist substance is left in contact with air, and in the course of a few hours a considerable portion will be insoluble in dilute hydrochloric acid and consist of oxyepiberberine.

Completely satisfactory results were obtained in investigating the conversion of epiberberinium sulphate into oxyepiberberine and dihydroanhydroepiberberine by the action of concentrated sodium hydroxide. This decomposition is analogous to that described in the case of the action of sodium hydroxide on berberinium sulphate (compare Gadamer, *loc. cit.*, pp. 35 and 36).

The sulphate (3 grams) is thoroughly mixed with sodium hydroxide (12 c.c. of 20 per cent.), the flask containing the mixture placed in cold water, and the water gradually raised to the boiling point and kept at this temperature for an hour. The product, which is not so dark-coloured as in the case of the corresponding experiment with berberinium sulphate, is diluted with much water, filtered by the aid of the pump, the ochreous powder washed and

then warmed with excess of very dilute hydrochloric acid, when dihydroanhydroepiberberine dissolves and a pale ochreous mass with a satiny lustre remains, which consists of nearly pure oxyepiberberine. This was thoroughly washed, dried in the steam-oven, dissolved in a little glacial acetic acid, and allowed to remain in a closed test-tube, when deep yellow needles of oxyepiberberine acetate separated. This was collected, washed with acetic acid, and dried between filter paper:

0.1368 gave 0.3221 CO_2 and 0.0641 H_2O . $\text{C}=64.2$; $\text{H}=5.2$.

$\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}$, $\text{C}_2\text{H}_4\text{O}_2$ requires $\text{C}=64.2$; $\text{H}=5.1$ per cent.

On exposure to moist air, this acetate gradually becomes opaque, owing to loss of acetic acid, and oxyepiberberine remains. The acetate is readily soluble in acetic acid, and if the solution is mixed with two volumes of boiling water, the clear liquid soon becomes filled with needles of oxyepiberberine. When the acetate is heated in a capillary tube, it becomes paler at about 110° and melts at $238-240^\circ$, the atmosphere of acetic acid having no effect on the melting point, which is that of oxyepiberberine. The acetate is quantitatively decomposed at $90-95^\circ$ into acetic acid and oxyepiberberine, as the following experiment shows:

1.2052 lost at $90-95^\circ$ 0.1736. $\text{C}_2\text{H}_4\text{O}_2=14.4$.

$\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}$, $\text{C}_2\text{H}_4\text{O}_2$ requires $\text{C}_2\text{H}_4\text{O}_2=14.6$ per cent.

The residue of pure oxyepiberberine was analysed:

0.1260 gave 0.3145 CO_2 and 0.0557 H_2O . $\text{C}=68.1$; $\text{H}=4.9$.

$\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}$ requires $\text{C}=68.3$; $\text{H}=4.8$ per cent.

Oxyepiberberine gradually darkens above 210° and melts approximately at $240-241^\circ$ to a dark brown syrup. It is very sparingly soluble even in boiling alcohol, and separates in well-developed rhombic plates, the angle of the rhomb being 66° ; in polarised light, diagonal extinction.

Dihydroanhydroepiberberine. The hot dilute hydrochloric acid filtrate which had been separated from the oxyepiberberine, as explained above, was mixed with more hydrochloric acid and left in the ice-chest, when it deposited a voluminous mass of slender, orange needles. This salt was collected, recrystallised from dilute hydrochloric acid, dissolved in hot water, and rendered alkaline with ammonia, when a milky liquid resulted which was extracted with much ether. After rapidly drying over potassium carbonate and concentrating, striated, lemon-yellow prisms separated, on keeping, which melted at 172° , and consisted of dihydroanhydroepiberberine (Found: $\text{C}=71.0$; $\text{H}=5.7$. $\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}$ requires $\text{C}=71.2$; $\text{H}=5.6$ per cent. Compare p. 508).

isoOxyepiberberine (compare p. 501).

The conversion of oxyberberine into *isooxyberberine* takes place gradually when the former is heated with dilute hydrochloric acid at 130° (Bland, Perkin, and Robinson, T., 1912, **101**, 264), but recent experiments have shown that the change occurs much more readily and completely when a temperature of 150–160° is employed.

In attempting to convert oxyepiberberine into *isooxyepiberberine*, the conditions originally employed in the case of the corresponding conversion of oxyberberine into *isooxyberberine* were adhered to, and the temperature was kept at 130° for five hours, but, on working up the contents of the sealed tube, practically the whole of the oxyepiberberine was recovered unchanged. Some slight action had taken place, because, on opening the tube, the liquid on the sides of the walls became coloured purple by the action of the air. When, however, the experiment was repeated at 150–160° for six hours, complete transformation had taken place. The contents of the tube were filtered by the aid of the pump, the residue washed and boiled out with glacial acetic acid, in which *isooxyepiberberine* is very sparingly soluble. The ochreous mass was then dissolved in boiling pyridine and filtered, when the substance separated as a voluminous mass of microscopic needles. It was collected, washed with hot methyl alcohol, and dried at 100°:

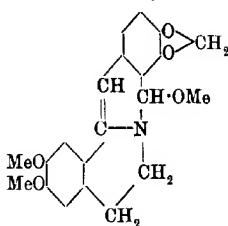
0.0984 gave 0.2473 CO₂ and 0.0448 H₂O. C=68.5; H=5.0.

C₂₀H₁₇O₅N requires C=68.4; H=4.8 per cent.

isoOxyepiberberine scarcely darkens at 270°, but gradually blackens at 300° without melting. It is almost insoluble in the usual solvents, including boiling glacial acetic acid, in which the isomeric *isooxyberberine* is comparatively readily soluble. A trace of the substance, rubbed on the sides of a test-tube, is coloured violet by sulphuric acid and dissolves to a pale brown solution; in the case of a similar experiment with nitric acid, the substance is coloured violet and dissolves to a deep bluish-violet solution, which becomes permanganate colour on the addition of water. When the suspension of the substance in alcohol is mixed with ferric chloride and warmed, a green colour develops. A very delicate reaction is obtained by dissolving a trace of *isooxyepiberberine* in boiling glacial acetic acid, cooling, and adding an equal volume of sulphuric acid. The addition of a drop of dilute nitric acid to the pale yellow solution produces a most intense violet coloration, and this, on dilution with water, becomes magenta. *isoOxy-*

berberine is insoluble in aqueous or alcoholic alkali even on boiling (compare *loc. cit.*, p. 264), but *isooxyepiberberine* is coloured deep brown by methyl-alcoholic potassium hydroxide, and dissolves, on warming, to a brown solution, from which a crystalline substance—probably a potassium salt—separates. On the addition of water, a brown solution is produced, from which acids liberate a flocculent precipitate. It appears, therefore, that *isooxyepiberberine* is more readily hydrolysed than is *isooxyberberine*. The addition of benzenediazonium chloride to the brown alkaline solution in aqueous alcohol gives, at first, a rather feeble brownish-red colour, but, on warming, this becomes very intense.

O-Methylepiberberine,



O-Ethylepiberberine, and Anhydroepiberberine-acetone.

O-Methylepiberberine is readily prepared from *epiberberinium* chloride or sulphate, either by the action of methyl-alcoholic potassium hydroxide or of sodium methoxide, and of these the latter is to be preferred.

(1) *epi*Berberinium chloride loses its brilliant colour when it is mixed with methyl-alcoholic potassium hydroxide (10 per cent.), and a pale drab, crystalline precipitate separates, especially on warming gently.

This was collected, washed with methyl alcohol, then with water, and again with methyl alcohol, and found to consist of practically pure *O*-methylepiberberine. For the analysis given below, a little of it was rapidly recrystallised from methylal, from which it separated in yellowish-brown prisms.

(2) The best method for preparing the *O*-methyl derivative is the following: *epi*Berberinium chloride (2 grams), suspended in methyl alcohol, is heated on the steam-bath, sodium (1 gram) dissolved in methyl alcohol added, and the whole rapidly filtered. Crystallisation begins at once, and pure *O*-methylepiberberine separates in a most beautiful manner in glistening, old-gold prisms. After remaining until cold, these were collected and washed with methyl alcohol.

The following analyses were made with specimens obtained from each of the above methods of preparation:

- (1) 0.1088 gave 0.2723 CO₂ and 0.0570 H₂O. C=68.3; H=5.8.
 (2) 0.1111 " 0.2798 CO₂ " 0.0582 H₂O. C=68.7; H=5.8.
 C₂₁H₂₁O₅N requires C=68.6; H=5.7 per cent.

O-Methylepiberberine melts at about 150—152° with decomposition to a black froth. Attempts to recrystallise it with the object more particularly of obtaining crystals suitable for measurement and comparison with *O-methylberberine* were unsuccessful. This is mainly due to the fact that the substance undergoes decomposition on boiling with such solvents as methylal or methyl alcohol, and a substance separates which melts at about 230—240°, and was readily identified as *oxypiberberine* (p. 518). *O-Methylepiberberine* is immediately converted by dilute hydrochloric acid into a deep orange-red salt which crystallises from dilute hydrochloric acid in brilliant orange needles, gives no precipitate when ammonia is added to its aqueous solution, and consists of *epiberberinium* chloride.

O-Ethylepiberberine, C₂₀H₁₈(OEt)₂O₄N, is prepared in a similar manner to the *O-methyl* derivative by boiling *epiberberinium* chloride with alcohol, adding excess of sodium ethoxide, and immediately filtering by the aid of the pump, when, on keeping in the ice-chest, circular, crystalline masses soon begin to form. After twenty-four hours, these were collected, washed first with alcohol, then with water, and dried at 80°:

0.1109 gave 0.2808 CO₂ and 0.0598 H₂O. C=69.1; H=6.0.

C₂₂H₂₃O₅N requires C=69.3; H=6.0 per cent.

O-Ethylepiberberine melts and decomposes at about 135—136°, and is sparingly soluble in boiling alcohol, from which it separates in groups of striated needles. It is apparently not so readily converted into *oxypiberberine* as the corresponding *O-methyl* derivative. It dissolves readily in boiling dilute hydrochloric acid, and *epiberberinium* chloride separates on cooling.

Anhydroepiberberine-acetone, C₂₀H₁₈(CH₂·COMe)₂O₄N. — *O-Methylepiberberine* dissolves readily in boiling acetone, and, if the solution is concentrated and set aside, a crust of yellow prisms of *anhydroepiberberine-acetone* gradually separates, but this substance does not crystallise with the same facility nor is it so highly characteristic as *anhydroberberine-acetone*. After recrystallisation from acetone, the substance melted not very sharply at about 162° and gave the following results on analysis:

0.1107 gave 0.2846 CO₂ and 0.0586 H₂O. C=70.1; H=5.9.

C₂₃H₂₃O₅N requires C=70.2; H=5.9 per cent.

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XI.III.—*Water-in-oil Emulsions.*

By ALFRED ULRICH MAX SCHLAEFFER.

With a system consisting of two liquid phases, *A* and *B*, it is theoretically possible to obtain two classes of emulsions, namely, *A*-in-*B* emulsions, in which *A* is the disperse phase and *B* the medium, and *B*-in-*A* emulsions, in which *B* is the interior and *A* the exterior phase (compare Wo. Ostwald, *Kolloid Zeitsch.*, 1910, 6, 103).

At first, the power of producing emulsions was exclusively attributed to substances which, when dissolved in one of the liquid phases, reduce the tension on their interface, thus facilitating the dispersion of one of them in the other.

Pickering (T., 1907, 91, 2001) was the first to prove that it is possible to obtain emulsions of hydrocarbon oils in water by means of solid emulsifiers, such as precipitates of basic copper sulphate, basic iron sulphate, etc., which are insoluble in either liquid and are moistened more by water than by the oil. He showed that the finely divided particles of the emulsifier form a coat over the oil droplets, preventing their coalescence. The action of the particles of hydrophile colloids, such as soap, etc., which had long been known as excellent emulsifiers, he considered to be similar to that of the grains of basic copper sulphate.

Pickering showed also that the type of an emulsion is largely independent of the proportions in which the two phases are present when he prepared emulsions of kerosene (disperse phase) in dilute soap solution (medium) containing up to 99 per cent. of kerosene in a 1 per cent. soap solution. Such emulsions, in which the disperse phase is greatly in excess over the medium, show an extremely high viscosity. Pickering did not consider the possibility of making emulsions of water in oil.

As Bancroft (*J. Physical Chem.*, 1912, 16, 475) pointed out in his discussion of Pickering's results, it is to be expected as their

corollary that insoluble particles, which are more easily moistened by oil than by water, will have a tendency to facilitate the emulsification of water in oil. In other words, if the solid particles of the emulsifiers have a lower surface tension with the phase *A* than with the phase *B*, it is to be expected that an emulsion will be formed with *A* as medium and *B* as disperse phase, and vice versa.

Newman (*J. Physical Chem.*, 1914, **18**, 34) found that soaps of certain alkaline earths, especially those containing magnesium, were excellent emulsifiers for emulsions of water in benzene. He showed also that mixed paints which contain a certain amount of water are to be considered as emulsions of the water-in-oil type. He drew the conclusion that in the latter case the emulsifying properties are to be ascribed to rosin and not to the pigment.

The experiments described below are concerned with the preparation of water-in-oil emulsions with the aid of a finely divided solid insoluble in both liquids, which is more easily wetted by the oil than by the water phase.

EXPERIMENTAL.

Materials Used.

Kerosene.—A water-white kerosene fraction (D_{40}^{20} 0.785) was redistilled over sodium. Distillation by Redwood's method gave the following result:

Distillate per cent.	0	10	20	30	40	50	60	70	80	90	95
Boiling point	156°	158°	160°	161°	166°	170°	174°	176°	182°	192°	208°

Carbon.—Best American carbon black (gas black, soot) was extracted for two days with hot benzene.

The distilled water was obtained from a tinned copper still.

The following experiments were carried out with these materials.

Experiment 1.—Thirty c.c. of water, 70 c.c. of kerosene, and 1 gram of carbon were shaken together in a flask. In this way, an emulsion was obtained which contained water as the disperse phase. This could easily be shown on a watch-glass by the fact that the emulsion mixed freely with kerosene, but not with water. Under a microscope, it was found that the droplets of water were covered with a dark brown skin of adsorbed particles of carbon. Those particles which were not adsorbed formed aggregates in the kerosene phase. The emulsion was liquid. After remaining for one day, it separated into pure kerosene, floating on the top, and a viscid emulsion which was still of the water-in-kerosene type and was stable for several weeks.

Experiment 2.—Seventy c.c. of water, 30 c.c. of kerosene, and

1 gram of carbon were shaken in a flask. In this, as in the other experiments here described, it was immaterial whether the carbon was added first to the water or to the oil or to both when mixed. The emulsion mixed freely with kerosene but not with water, and was therefore again of the water-in-oil type. It was so viscid that it did not flow out of a reversed test-tube. It kept for more than a week without altering.

To show the influence of the quantitative proportions of the two phases more clearly, experiments were made in order to determine the time of flow of the emulsions from a 5 c.c. pipette. For the same pipette (all experiments were carried out at about 18°), water required on an average 3.3 seconds and the kerosene 3.5 seconds. The results of these experiments are shown in the table on p. 525.

In this case, the emulsions were prepared in the manner recommended by Pickering, by alternately filling and emptying a garden syringe. The number of strokes, which is a crude criterion of the amount of mixing, has a certain influence on the viscosity of the mixture. The table clearly shows the enormous increase of viscosity which is produced by an increasing proportion of the inner phase.

In experiments 7 and 8, it was not possible to get all the water into the emulsion. It is worth special notice that neither in these nor in any other similar experiments was it ever possible to obtain an emulsion of kerosene in water with the aid of carbon. When the amount of water was too large to be carried by the kerosene, an emulsion with less water was formed, together with an unaltered residuum of water. Since the size of droplets occurring together changed within a large range, especially in the emulsions containing a large amount of water, it does not seem justifiable to make any speculations on the fact that the limit of stability under the described conditions was about 70. per cent. water-content (compare Wo. Ostwald, *loc. cit.*). More water could be added by stirring, but in consequence of the considerable tension on the interface of the two liquids, the droplets stirred in were large. It might, of course, be possible to obtain emulsions of higher water-concentration with carbon black if a fourth compound were added to lower the surface tension between the two liquid phases.

Similar emulsions could be made in an analogous way, using turpentine, benzene, toluene, etc., instead of kerosene.

It may be stated that carron oil, the well-known liniment for burns which is prepared with lime-water and linseed or rape oil, is an emulsion of the water-in-oil type, whilst embrocations are well known to be of the oil-in-water type.

Carron oil mixes freely with organic solvents, but not with water

No of Expt.	Quantities used.		Time required for emulsion to flow out of 5 c.c. pipette* (Means of 9 experiments each)			Amount of kerosene in c.c. floating on top of 100 c.c. of emulsion after twenty- four hours.	Percentage of water in residual emulsion after twenty-four hours.	REMARKS.
	Kerosene, c.c.	Water, c.c.	Carbon, grams.	After 160 strokes with syringe.	After 320 strokes with syringe.	After 480 strokes with syringe.		
3	240	60	1.5	4.4	4.7	5.3	48	38.5
4	180	120	1.5	7.4	7.8	—	not measured	—
5	120	180	1.5	—	26	44	11	67.5
6	90	210	1.5	Did not flow out of pipette or from reversed test-tube.			none	—
7	60	240	1.5	Emulsified part did not flow out of pipette or a reversed test-tube.			It was not possible to emulsify all the water in the experi- ments. An emulsion of water in kerosene was obtained besides pure water. No emulsion of kerosene in water could be obtained.	
8	60	240	3.0					

* As marks, the 5 c.c. mark on the upper tube and the beginning of the lower tube at the bottom of the bulb were taken.

without shaking, and easily dissolves oil colours, but not dyes soluble in water.

Summary.

(1) It is possible to make emulsions of water as disperse phase in organic solvents with the aid of finely divided carbon as emulsifier.

(2) The carbon particles, without leaving the oil phase, form a skin over the water droplets, preventing their coalescence.

(3) The order in which the ingredients are added does not make any difference to the final product.

(4) The emulsions obtained in this way are the more viscous the more water they contain.

(5) Carron oil is a water-in-oil emulsion.

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XLIV.—*The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. The Influence of certain Inorganic Haloids on the Optical Rotatory Powers of α -Hydroxy-acids, α -Amino-acids, and their Derivatives.*

By GEORGE WILLIAM CLOUGH.

The Walden Inversion.

THE discovery of the phenomenon known as the Walden inversion was made in connexion with transformations of certain derivatives of succinic acid, and it therefore seemed possible that the change of configuration was due either to the presence of an atom of hydrogen attached to the asymmetric carbon atom or to the fact that the optically active compounds in question were carboxylic acids. Although the configurative change may be due to one or both of these causes in certain cases, it has been shown that a Walden inversion can be effected in a compound containing a tertiary asymmetric carbon atom (McKenzie and Clough, T., 1910, 97, 1016), and also in compounds which do not contain a carboxyl

group. In his studies on this phenomenon, Fischer observed that the action of a reagent on an ester frequently yielded a compound of the enantiomorphous configuration to that of the compound produced by the same reagent on the corresponding acid, and in such examples he assumed that the action on the ester was not accompanied by change of configuration. That an inversion is possible in the case of an ester has been shown by the fact that phosphorus pentachloride and thionyl chloride yield chloro-esters of opposite signs when they react with the same optically active ethyl α -phenyl-lactate (McKenzie and Clough, T., 1910, **97**, 2564). Further, it is not necessary that the optically active compound should contain either a carboxyl or carbalkyloxy-group, for it has been found possible to effect the interconversion of the optically active phenylmethylcarbinols (T., 1913, **103**, 687).

Several attempts have been made to decide in which reactions an inversion occurs by employing certain assumptions regarding the mechanism of the reactions in question (Armstrong, T., 1896, **69**, 1399; Gadamer, *Chem. Zeit.*, 1910, **34**, 1004; 1912, **36**, 1327; Billmann, *Annalen*, 1911, **388**, 338). It has been shown that Billmann's hypothesis cannot be applied to all the examples which have been investigated (McKenzie and Clough, *loc. cit.*), and, moreover, Senter and Drew's experiments (T., 1916, **109**, 1091) concerning the influence of the solvent on the rotatory sign of the phenylaminoacetic acids produced by the action of ammonia on the active phenylchloroacetic acids emphasise the difficulty of drawing conclusions regarding the specific action of a reagent from considerations of the probable mechanism of the reactions. It may still be said that "there does not exist at the present time any criterion whereby the relation between the configuration of an optically active compound and that of a derivative from it can be decisively ascertained" (Frankland, T., 1913, **103**, 738).

Accordingly, it seemed desirable that the problem should be investigated by an entirely different method. The present author has therefore made experiments with the object of ascertaining whether the measurements of the rotatory powers of similarly constituted compounds would reveal regularities between the rotatory values and the relative configurations of the active compounds. In such an investigation, it is necessary to consider the influence of the conditions (temperature, solvent, and concentration) on the rotatory powers of each compound, and also to study the relative effects of substituents introduced into the groups attached to the asymmetric carbon atom. It would, indeed, be impossible to draw a sharp distinction between these two methods of procedure if the assumption is made that some solvents form labile compounds

with the active solute (compare Walden, *Ber.*, 1905, **38**, 408). When it is also recalled that the work of Pickard and Kenyon has brought to light surprising regularities when the rotations of derivatives from a given compound are measured for light of different wave-lengths, it is evident that an entirely satisfactory comparison of the optical rotatory powers of two parent compounds can be made only when the rotatory powers of the compounds and their derivatives have been measured under many varying conditions. Fortunately, the labours of Frankland, Guye, Purdie, Patterson, Walden, and others have resulted in the accumulation of much data available for a comparison of the rotatory powers of the common optically active aliphatic α -hydroxy-acids, whilst the publications of Fischer contain rotation constants for the majority of the active α -amino-acids. The measurements made by the author are by no means as comprehensive as could be wished, but it appears desirable to place on record the results which have been obtained for several α -hydroxy- and α -amino-acids, and to discuss these from the above point of view, especially as conclusions have been drawn concerning the relative configurations of compounds of the sugar series from a consideration of their rotatory powers (Hudson, *J. Amer. Chem. Soc.*, 1917, **39**, 462). In the present paper, attention is directed particularly to regularities observed in the effect of temperature and of certain inorganic haloids on the optical rotatory powers of some α -hydroxy- and α -amino-acids and esters in aqueous or methyl-alcoholic solution.

α -Hydroxy-acids and their Derivatives.

In previous communications (I., 1914, **105**, 49; 1915, **107**, 96, 1509), it has been established that the optical rotatory powers of configuratively similar hydroxy-derivatives of succinic acid containing a carboxyl or carbalkyloxy-group are influenced in the same sense by the presence of the haloids of the alkali or alkaline earth metals in aqueous solutions. These salts diminish considerably the numerical values for the specific rotatory powers and frequently reverse the sign of rotation. With the view of ascertaining whether other hydroxy-acids and esters are, in this respect, similar to malic and tartaric acids, the author has examined the rotatory powers of *l*-lactic acid, methyl *l*-lactate, and *d*-glyceric acid in aqueous solution and in aqueous solutions of certain neutral salts. It is well known that *l*-lactic acid, which is levorotatory in aqueous solution, yields dextrorotatory salts and esters. The levorotatory power of this acid in aqueous solution diminishes with rise of temperature, and is ultimately reversed. The influence of temperature on the

optical rotatory power of *l*-lactic acid in aqueous solution is thus similar to that on methyl *l*-lactate in the homogeneous condition, for Patterson and Forsyth observed that rise of temperature increases the dextrorotatory power of this ester (T., 1913, 103, 2263). The presence of sodium or barium haloids increases the laevorotatory power of *l*-lactic acid (table I), and similarly the dextrorotatory power of methyl *l*-lactate in aqueous solution is diminished or reversed by the salts employed (table II). The rotatory values being usually small, the measurements recorded are for mercury-green light ($\lambda=5461$).

TABLE I.

The Influence of Sodium Chloride, Sodium Bromide, and Barium Bromide on the Optical Rotatory Power of l-Lactic Acid in Aqueous Solution.*

Salt.	Grams of salt added to 25 c.c. of solution.	p .	d^{20} .	α_{20}^{10} ($l=4$).	$[\alpha]_D^{20}$.
None	—	10.73	1.027	— 0.95°	— 2.2°
Sodium chloride	5.85	8.71	1.182	— 3.08	— 7.6
Sodium bromide	10.30	7.65	1.293	— 3.16	— 8.0
Barium bromide	14.80	6.79	1.485	— 7.10	— 17.7

* This specimen contained 8 per cent. of *d*-lactic acid.

TABLE II.

The Influence of Inorganic Salts on the Optical Rotatory Power of Methyl l-Lactate in Aqueous Solution.*

Solvent.	p .	d^{20} .	α_{20}^{20} ($l=2$).	$[\alpha]_D^{20}$.
None	100	1.093	+ 18.34°	+ 8.4°
Water	10.0	1.012	+ 0.29	+ 1.4
Aqueous sodium chloride (N)	10.0	1.050	+ 0.11	+ 0.5
" " " (4-N) ...	10.37	1.150	— 0.50	— 2.1
" sodium bromide (N).....	10.0	1.080	+ 0.10	+ 0.5
" potassium chloride (N) ...	10.0	1.054	+ 0.10	+ 0.5
" ammonium chloride (N) ...	10.0	1.027	+ 0.19	+ 0.9
" calcium chloride (N)	10.0	1.054	— 0.22	— 1.0
" barium chloride (N)	10.0	1.094	— 0.28	— 1.3
" barium bromide (4-N) ...	9.81	1.456	— 2.60	— 9.1

* This specimen contained 5 per cent. of methyl *d*-lactate.

Notwithstanding the fact that the influence of water on the rotatory power of methyl *l*-lactate is opposite in sense to that of this solvent on the esters of *d*-malic acid or *d*-tartaric acid, it is obvious that the changes of rotation caused by the inorganic haloids are the same in character for *l*-lactic acid and methyl *l*-lactate as

for the configuratively similar compounds *d*-tartaric acid and methyl *d*-tartrate. On the other hand, the changes observed in the case of *d*-glyceric acid are opposite in character to those for *L*-lactic acid. Frankland and Frew have shown that *d*-glyceric acid is dextrorotatory in aqueous solution at the ordinary temperature, but that the specific rotation $[\alpha]_D$ becomes zero in dilute solution (T., 1891, **59**, 96); moreover, this acid yields levorotatory salts and esters (T., 1893, **63**, 297, 511, 1410). The author finds that *d*-glyceric acid in aqueous solution becomes levorotatory on raising the temperature, and that the addition of certain inorganic haloids increases the rotation of the acid (table III).

TABLE III.

The Influence of Sodium Chloride and Barium Chloride on the Optical Rotatory Power of d-Glyceric Acid in Aqueous Solution.

Salt.	Grams of salt added to 25 c.c. of solution.	<i>p</i> .	<i>d</i> ₂₀ .	$\alpha_{gr}^{20} (l=2)$.	$[\alpha]_D^{20}$.
None	—	2.40	1.01	$\pm 0.00^\circ$	$\pm 0.0^\circ$
Sodium chloride	5.85	1.84	1.17	+ 0.21	+ 4.9
Barium chloride	5.20	1.90	1.22	+ 0.32	+ 6.9

The earlier experiments of Stubbs (T., 1911, **99**, 2265), Patterson and Anderson (T., 1912, **101**, 1833), and the present author concerning the influence of neutral salts on the optical rotatory powers of certain compounds in solution were made with aqueous solutions. Patterson and Anderson, however, found that the dissolution of certain salts in homogeneous ethyl tartrate depressed the rotation of this ester. Walden observed that ethyl tartrate ($\alpha_D^{13} + 6.1^\circ$, $l=1$), after saturation with hydrogen bromide, gave $\alpha_D^{18} - 7.0^\circ$ ($l=1$) (Ber., 1905, **38**, 407). It has now been found that the dissolution of about 5 per cent. of calcium chloride in methyl *L*-lactate depresses the rotation from $\alpha_{gr}^{15} + 8.55^\circ$ to $\alpha_{gr}^{13} + 5.5^\circ$ ($l=1$). In this connexion, it should be stated that a solution of calcium chloride in this ester readily deposits a crystalline compound of the formula $\text{CaCl}_2 \cdot 4\text{C}_4\text{H}_8\text{O}_5$ (Found: Cl=13.4. Calc.: Cl=13.5 per cent.). A similar compound of calcium chloride with ethyl lactate has been described by Strecker (*Annalen*, 1854, **91**, 355). Measurements of the rotatory powers of several compounds dissolved in methyl alcohol and in methyl alcohol containing sodium bromide show that the effect of this salt is even greater in methyl alcohol than in water (table IV).

TABLE IV.

The Influence of Sodium Bromide on the Optical Rotatory Powers of l-Malic Acid, d-Tartaric Acid, Methyl l-Lactate, Methyl l-Malate, and Methyl d-Tartrate in Methyl-alcoholic Solution.

Compound.	$[\alpha]_D^{25}$ (in methyl alcohol, $c=10$).	$[\alpha]_D^{25}$ (in methyl- alcoholic sodium bromide, $N, c=10$).
<i>l</i> -Malic acid	- 5.9°	+ 21.8°
<i>d</i> -Tartaric acid	+ 2.6	- 9.0
Methyl <i>l</i> -lactate	+ 5.4	- 5.8
Methyl <i>l</i> -malate	- 9.4	+ 9.1
Methyl <i>d</i> -tartrate	+ 2.7	- 12.6

It is of interest to note that sodium bromide exerts a distinct influence on the rotatory powers of the methyl and ethyl esters of *d*-diacetoxy succinic acid in methyl-alcoholic solution, but the effect observed is opposite in character to that of the same salt on the corresponding esters of *d*-tartaric acid. Methyl *d*-diacetoxy-succinate gave $[\alpha]_D^{25} - 18.3^\circ$ in methyl alcohol ($c=4$), whilst in *N*-methyl-alcoholic sodium bromide the value was $[\alpha]_D^{25} - 12.2^\circ$ ($c=4$); similarly, for ethyl *d*-diacetoxy succinate the values obtained were $[\alpha]_D^{25} + 3.6^\circ$ ($c=5$) and $[\alpha]_D^{25} + 7.6^\circ$ ($c=5$) respectively. It thus appears that the specific effect of salts on the optical rotatory powers of hydroxy-acids and esters is due to the presence of alkyl hydroxyl groups in these compounds.

Now, Freudenberg (*Ber.*, 1914, **47**, 2037) has shown that the four hydroxy-acids, *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid, all possess the same relative configurations, that is to say, the hydrogen atoms, the hydroxyl and carboxyl groups attached to the asymmetric carbon atoms have a similar spatial disposition in the molecules of these compounds. These relationships have been proved by transformations which do not involve replacements of groups directly attached to the asymmetric carbon atom, and inasmuch as no example is known in which such a change produces inversion, it is justifiable to assume that no configurative change occurs in these reactions. When the rotatory powers of these four acids and of their derivatives are compared, the regularities observed are extremely striking and significant, especially when it is remembered that malic and tartaric acids are dibasic (and may thus be regarded also as β -hydroxy-acids), and that tartaric acid contains two adjacent asymmetric carbon atoms. It has been shown by the author that the influence of temperature on the rotatory powers of these related acids* in aqueous solution

* *l*-Malic acid was examined, but the discussion is simplified by reference to *d*-malic acid.

is similar in character for the four compounds, the dextrorotation being increased (or the levorotation diminished) in each case. The rotations are also increased by dilution, and the molecular rotations of the sodium or potassium salts in aqueous solution are in each case higher (that is, more positive) than those of the free acids in aqueous solution. Further, the presence of inorganic haloids influences the rotatory powers of the acids in aqueous solution in the same sense.

Similar regularities are observed on examination of the rotatory values of the esters of these acids. Thus the temperature-rotation curves for methyl *l*-lactate (Patterson and Forsyth, *loc. cit.*), methyl *l*-glycerate (Frankland and McGregor, T., 1894, 65, 768), methyl *d*-malate (Clough, T., 1915, 107, 103), and methyl *d*-tartrate (Pictet, *Jahresber.*, 1882, 855) are all similar in character. The molecular rotations of the esters, which are higher than those of the parent acids (calculated, where possible, by extrapolation), increase, in the case of the lower members of the homologous series, with increase of molecular weight. The influence of a given solvent on the rotations of esters of the configuratively related acids, *d*-tartaric acid, *d*-malic acid, and *l*-lactic acid, is in general the same in character, the elevating effect of aromatic nitro-compounds and the depressing effect of aliphatic halogen compounds being particularly striking. It must be stated that there are a few important exceptions to this rule. The regularities observed when inorganic salts are dissolved in solutions of esters of the acids in question are well illustrated by table IV. It therefore appears that, in general, changes of the same character are brought about in the optical rotatory powers of the similarly con-

TABLE V.

The Influence of Substituents on the Molecular Rotations [M]_D of l-Lactic Acid, l-Glyceric Acid, d-Malic Acid, and d-Tartaric Acid.

	Y = H.	Y = Me.	Y = Et.
$l\text{-CH}_3\text{-CH(OH)-CO}_2\text{Y}$	- 2° (H ₂ O, c = 5)	+ 8.6°	+ 12.2°
$l\text{-CH}_2\text{(OH)-CH(OH)-CO}_2\text{Y}$	- 2.3 (H ₂ O, c = 20)	+ 5.8	+ 12.3
$d\text{-CO}_2\text{Y-CH}_2\text{-CH(OH)-CO}_2\text{Y}$...	- 6.3*	+ 11.1	+ 19.8
$d\text{-CO}_2\text{Y-(CH-OH)}_2\text{-CO}_2\text{Y}$	- 4.2*	+ 3.8	+ 15.9
	X = Ac, Y = Et.	X = Bz, Y = Me.	X = Me, Y = Me.
$l\text{-CH}_3\text{-CH(OX)-CO}_2\text{Y}$	+ 79.7°	- 59.0°	+ 112.7°
$l\text{-CH}_2\text{(OX)-CH(OX)-CO}_2\text{Y}$	+ 35.6	- 89.2	+ 103.5
$d\text{-CO}_2\text{Y-CH}_2\text{-CH(OX)-CO}_2\text{Y}$	+ 52.3	+ 11.4	+ 92.4
$d\text{-CO}_2\text{Y-(CH-OX)}_2\text{-CO}_2\text{Y}$	+ 10.0	- 123.6	+ 180.0

* By extrapolation, Winther, *Zeitsch. physikal. Chem.*, 1902, 41, 181; or other references, see Frankland and Gebhard, T., 1905, 87, 865.

stituted optically active α -hydroxy-acids possessing the same relative configurations by similar alterations of temperature, by dissolution in a given solvent, or by the addition of a given optically inactive substance to solutions of the active compounds. Further, it is evident from table V that the introduction of a given radicle into the molecules of the configuratively similar hydroxy-acids in question usually produces alterations of the same character in the rotatory powers.

It should now be possible to determine the relative configurations of similar α -hydroxy-acids with reference to *d*-tartaric acid, but unfortunately in no case are the available data so comprehensive as in the above examples. A comparison of the values for derivatives from *l*- α -hydroxybutyric acid (Guye and Jordan, *Compt. rend.*, 1895, **120**, 1274) with those in table V indicates that *l*- α -hydroxybutyric acid possesses a configuration similar to that of *l*-tartaric acid.

	X=H, Y= NH ₄	X=H, Y= Et.	X=H, Y= isoBu.	X=Ac, X=Bz, Y= isoBu.	Y= isoBu.
$l\text{-C}_4\text{H}_7\text{CH(OX)-CO}_2\text{Y}$ [M] _D	-16.8° (H ₂ O)	-2.5°	-12.3°	-62.0°	+3.2°

The author has examined the influence of sodium chloride (or bromide) on *d*- β -phenyl-lactic acid and its methyl ester (table VI) with results which, taken in conjunction with those in table IV, show that this acid is related configuratively to *d*-tartaric acid.

TABLE VI.

The Influence of Sodium Haloids on the Optical Rotatory Powers of d- β -Phenyl-lactic Acid and Methyl d- β -Phenyl-lactate in Solution.

Compound.	Solvent.	c.	t.	α_D^{20} (l=2).	$[\alpha]_D^{20}$.
<i>d</i> - β -Phenyl-lactic acid ...	Water	2.505	20°	+ 1.28°	+ 25.5°
" " " ...	Aqueous sodium chloride (4 <i>N</i>)	0.665	20	+ 0.18	+ 13.5
" " " ...	Methyl alcohol	10.0	20	+ 4.20	+ 21.0
" " " ...	Methyl-alcoholic sodium bromide (N)	10.0	20	- 0.41	- 2.0
Methyl <i>d</i> - β -phenyl-lactate	Methyl alcohol...	10.0	18	- 0.90	- 4.5
" " " ...	Methyl-alcoholic sodium bromide (N)	10.0	18	- 4.46	- 22.3

The values for *l*- α -hydroxyisohexoxic acid calculated from the results of Scheibler and Wheeler (*Ber.*, 1911, **44**, 2684) are $[\text{M}]_D^{20}$ -13.7° (in water) and $[\text{M}]_D^{20}$ -36.7° (in *N*-sodium hydroxide), whilst the ethyl ester gives $[\text{M}]_D^{20}$ -18.3°. Fischer and Moreschi (*Ber.*, 1912, **45**, 2447) find that *l*- α -hydroxyglutaric acid is feebly

lævorotatory in aqueous solution at 18°, and that the sodium salt gives $[M]_D^{20} - 14.6^\circ$. On the other hand, whilst *l*- α -hydroxy^{iso}-valeric acid is slightly lævorotatory in aqueous solution, the zinc salt in *N*-sodium hydroxide gives $[M]_D^{20} + 35.4^\circ$ (Fischer and Scheibler, *Ber.*, 1908, **41**, 2891). It thus seems very probable that *l*- α -hydroxy^{iso}-valeric acid possesses the same configuration as *d*-tartaric acid, but that *l*- α -hydroxy^{iso}-hexoic acid and *l*- α -hydroxy-glutaric acid are enantiomorphously related to this acid. The conclusion is therefore drawn that *l*-lactic acid,* *l*-glyceric acid, *d*-malic acid, *d*- α -hydroxybutyric acid, *l*- α -hydroxy^{iso}-valeric acid, *d*- α -hydroxy^{iso}-hexoic acid, *d*- α -hydroxyglutaric acid, and *d*- β -phenyl-lactic acid all possess the same relative configurations as *d*-tartaric acid. These optically active acids will be referred to in the sequel as "*d*". and their optical antipodes as "*l*"-aliphatic α -hydroxy-acids.

The remarkable effect on rotatory power which has been frequently noticed when a phenyl group is attached to the asymmetric carbon atom rendered it advisable to compare the influence of salts on the rotatory power of such a compound with that exerted on aliphatic compounds. Sodium chloride was found to increase the lævorotatory power of *l*-mandelic acid in aqueous solution from $[\alpha]_D^{18} - 188^\circ$ ($c=1.6$) to $[\alpha]_D^{18} - 203^\circ$ (4*N*-sodium chloride, $c=1.6$), and sodium bromide had a similar effect on ethyl *l*-mandelate, which gave $[\alpha]_D^{18} - 141^\circ$ in methyl alcohol ($c=10$) and $[\alpha]_D^{18} - 181^\circ$ in *N*-methyl-alcoholic sodium bromide ($c=10$). If the rules which have been established from a study of the simple aliphatic α -hydroxy-acids may be applied when a phenyl group is attached to the central carbon atom, it would follow that *l*-mandelic acid is related to *d*-tartaric acid. This conclusion receives support on reference to the rotations of some derivatives (esters, amide) from *l*-mandelic acid. The lævorotatory power of *l*-mandelic acid in aqueous solution diminishes on dilution, and the salts possess numerically lower molecular rotations than the free acid in aqueous solution. The lævorotatory powers of the acid in aqueous solution (Lewkowitsch, *Ber.*, 1883, **16**, 1567) and of the esters in the pure condition (J. W. Walker, *J. Physical Chem.*, 1909, **13**, 574) diminish with rise of temperature, and the molecular rotatory powers of the esters decrease numerically with increase of molecular weight—methyl ester $[M]_D^{20} - 276^\circ$, ethyl ester $[M]_D^{20} - 226^\circ$ (J. W. Walker, *loc. cit.*), isobutyl ester $[M]_D^{20} - 209^\circ$ (Walden, *Zeitsch. physikal. Chem.*, 1895, **17**, 706). In all these respects, the behaviour of *l*-mandelic acid is opposite to that of *l*-malic acid.

* In this paper, the designations (*d*- or *l*-) of the optically active compounds mentioned are those usually given in the literature, and are not used to indicate the relative configurations of the compounds.

It must be repeated that the employment of this method cannot be regarded as wholly satisfactory unless the compounds and their derivatives are examined in a systematic manner under varying conditions, but it is shown later that there is confirmatory evidence that the conclusions which have been drawn with regard to the configurations of the active aliphatic α -hydroxy-acids are in all probability correct. It may be recalled that Frankland and Turnbull have shown the configurative relationships of the optically active esters of $\alpha\beta$ -dichloropropionic acid by investigating the effect of temperature on their rotatory powers (T., 1914, **105**, 456), and that the present author has discussed the relative configurations of the optically active normal secondary alcohols on the basis of their optical rotation constants determined by Pickard and Kenyon (P., 1913, **29**, 357. Compare Kenyon, T., 1914, **105**, 2232). Pickard and Kenyon have suggested the employment of a "characteristic diagram" (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, [A], **88**, 388) for determining whether a change of configuration has taken place in the formation of a derivative (P., 1913, **29**, 296).

α -Amino-acids and their Derivatives.

The author has previously shown that the optical rotatory powers of *l*-asparagine and *l*-aspartic acid are very susceptible to the influence of inorganic salts (T., 1915, **107**, 1509). Pfeiffer subsequently obtained similar results for *d*-alanine, the dextrorotatory power of which in aqueous solution is raised by the dissolution of lithium chloride or calcium chloride; thus, the addition of 5 grams of calcium chloride to 10 c.c. of an aqueous solution of *d*-alanine (10 per cent.) raised $[\alpha]_D$ from $+2.10^\circ$ to $+11.85^\circ$ (Ber., 1915, **48**, 1938). For the sake of comparison with *l*-aspartic acid, the present author has determined the rotations of *d*-alanine in aqueous solutions of other salts (table VII).

TABLE VII.

The Influence of Inorganic Salts on the Optical Rotatory Power of d-Alanine in Aqueous Solution.

Solvent.	<i>c</i>	$\alpha_D^{15} (l=2)$.	$[\alpha]_D^{15}$.
Water	10.0	$+0.58^\circ$	$+2.9^\circ$
aqueous potassium chloride (N)	10.0	0.61	3.0
" sodium chloride (N)	10.0	0.66	3.3
" barium chloride (N)	10.0	0.70	3.5
" barium bromide (4N)	10.0	0.96	4.8
" hydrogen chloride (1.5 mols.)	5.78	2.06	17.8

Inasmuch as these results are similar to those observed for aspartic acid, which is dextrorotatory in aqueous solution at the

ordinary temperature, but becomes levorotatory at higher temperatures, the influence of temperature on the rotatory power of *d*-alanine in aqueous solution has been studied and found to be quite similar to that on *L*-aspartic acid, a reversal in the sign of rotation being realised at about 70°.

The investigation has been extended to *d*-glutamic acid. The optical behaviour of this compound is parallel to that of *L*-aspartic acid; both these compounds are dextrorotatory in aqueous solution at the ordinary temperature, and elevation of temperature depresses the rotatory values, but whereas *L*-aspartic acid becomes levorotatory at about 60°, it was not found possible to reverse the rotatory sign of *d*-glutamic acid in aqueous solution. The presence of neutral or acid salts in solution increases the dextrorotatory power of *d*-glutamic acid (table VIII).

TABLE VIII.

The Influence of Inorganic Salts on the Optical Rotatory Power of d-Glutamic Acid in Aqueous Solution.

Solvent.	<i>p</i> .	<i>d</i> ₂₅ ²⁵ .	$\alpha_{\text{D}}^{25}(l=1)$.	$[\alpha]_{\text{D}}^{25}$.
Water	1.50	1.003	+ 0.80°	+ 13.3°
Aqueous sodium chloride (N)	1.50	1.043	0.90	14.4
" " (4N)	1.51	1.152	1.10	15.8
" potassium chloride (N)	1.53	1.050	0.95	14.8
" barium chloride (N)	1.53	1.092	0.96	14.4
" barium bromide (4N)	1.51	1.500	1.64	18.1
" sodium hydroxide (1 mol.)	12.25	1.075	- 1.88	- 3.6
" " (2 mols.)	6.55	1.050	+ 3.22	+ 11.7
" hydrogen chloride (1.5 mols.)	8.75			+ 37.4

A comparison of the rotatory powers of hydroxy-acids with those of their esters in the presence of neutral salts having shown that both classes of compounds are influenced in a similar manner, it was advisable to examine polarimetrically an ester of an amino-acid under various conditions, especially as such an examination might possibly throw some light on the constitution of amino-acids in aqueous solution. Accordingly, ethyl *L*-aspartate has been examined in various solvents. The levorotatory power of this ester is increased by rise of temperature and reversed by dissolution in water or hydrochloric acid. The gradual addition of water (with which the ester is completely miscible) at first causes a rapid diminution of the levorotation until *p*=80, when the solution is dextrorotatory; further dilution after *p*=50 has very little influence on the specific rotation. The addition of sodium or barium haloids increases the dextrorotatory power of the ester in aqueous solution, and sodium bromide reverses the levorotatory power of the ester in methyl-alcoholic solution at 20°.

TABLE IX.

The Influence of Solvents on the Optical Rotatory Power of Ethyl L-Aspartate.

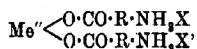
Solvent.	c.	$\alpha_{gr.}^{15} (l = 2).$	$[\alpha]_{gr.}^{15}.$
None		- 6.34° ($l = 0.5$)	- 11.7°
Benzene	10.92°	- 2.75	- 12.6
Chloroform	11.02	- 2.13	- 9.7
Acetone*	20.0	- 3.50	- 8.8
Water	21.7	+ 1.83	+ 4.2
Water	12.25	1.03	4.2
Aqueous sodium chloride (4N)	10.81	1.44	6.7
Aqueous barium bromide (4N)	14.50	3.34	11.5
„ calcium chloride (5N)	13.21	3.84	14.5
„ hydrogen chloride (N)	11.37	2.73	12.0
Methyl alcohol	20.0	$\alpha_{gr.}^{20} - 0.19$	$[\alpha]_{gr.}^{20} - 0.5$
Methyl-alcoholic sodium bromide (N)	20.0	$\alpha_{gr.}^{20} + 1.72$	$[\alpha]_{gr.}^{20} + 4.3$

* Ethyl L-aspartate reacts with acetone, the rotation changing from $\alpha_{gr.} - 3.50^\circ$ to $\alpha_{gr.} - 56.6^\circ$ ($c = 20$) in fifteen hours.

Finally, measurements made with benzoyl-*D*-alanine show that when the amino-group is displaced by the benzoylamino-group, the characteristic optical behaviour of the amino-acid disappears. For example, although benzoyl-*D*-alanine is only feebly dextrorotatory in aqueous solution ($[\alpha]_{gr.}^{15} + 0.3^\circ$, $p = 12$), little alteration could be detected on raising the temperature ($[\alpha]_{gr.}^{17} + 0.2^\circ$; the specific rotation is slightly higher in *N*-potassium chloride ($[\alpha]_{gr.}^{20} + 0.4^\circ$, $p = 11$), but this result is due to the fact that the potassium salt of benzoyl-*D*-alanine is much more dextrorotatory than the free acid in aqueous solution. It thus appears that the effect of neutral salts on the rotatory powers of amino-acids is due to the presence of the amino-group in these compounds.

Now the elevation of the rotation of ethyl L-aspartate by dissolution in hydrochloric acid or water is probably due to the nitrogen atom becoming quinquevalent ($\cdot\text{NH}_3\text{Cl}$, $\cdot\text{NH}_3\cdot\text{OH}$), and in the latter case there would probably exist in solution a mixture of the hydrated and non-hydrated forms of the amine. The rotatory values for the amino-acid and ester indicate similar constitutions in solution for both compounds, and it would thus appear that L-aspartic acid in aqueous solution consists mainly of the forms $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ and $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_3\cdot\text{OH})\cdot\text{CO}_2\text{H}$, the former being levorotatory and the latter dextrorotatory. The relative amount of the hydrated form would diminish with rise of temperature. Further work on the rotatory powers of amino-

acids and their esters would be of interest in this connexion. The presence of neutral salts influences not only the rotatory powers, but the solubilities of amino-acids and proteins in aqueous solution. Schiff (*Ber.*, 1884, **17**, 2929) observed that aspartic acid dissolves more readily in aqueous ammonium chloride than in water, and suggested that this was due to the amino-acid exercising its basic and acidic functions, the compounds yielding an equilibrium mixture of ammonium aspartate, aspartic acid hydrochloride, and unchanged ammonium chloride. Sakurai (P., 1894, **10**, 90) ascribed the formula $\text{CH}_2(\text{NH}_3\cdot\text{NO}_3)\cdot\text{CO}_2\text{K}$ to a compound of glycine with potassium nitrate described by Boussingault (*Annalen*, 1841, **39**, 310). Although unable to isolate this compound, Pfeiffer and von Modelski succeeded in preparing a large number of compounds of amino-acids with the haloids of the alkali and alkaline earth metals, and also regarded these compounds as "amphi" salts possessing the formulæ $\text{Me}\cdot\text{O}\cdot\text{CO}\cdot\text{R}\cdot\text{NH}_3\text{X}$ or



(*Zeitsch. physiol. Chem.*, 1912, **81**, 329; 1913, **85**, 1). This view was modified by Pfeiffer and Wittka, who regard the compounds of inorganic salts with amino-acids, carboxylic acids, esters, etc., as "molecular" compounds, without excluding the possibility that the halogen atom of the inorganic salt is combined with the amino-group of an amino-acid in the form of an ammonium salt (*Ber.*, 1915, **48**, 1289). Pfeiffer has also brought forward strong evidence that the compounds of amino-acids with neutral salts are capable of existence in aqueous solution (*Ber.*, 1915, **48**, 1938). Inasmuch as the amino-acids are amphoteric electrolytes possessing very small acid and basic constants (for alanine $K_a = 1.9 \times 10^{-10}$, $K_b = 5.1 \times 10^{-12}$), it does not seem possible for the halogen of the salts to be combined in the "ammonium" salt form, nor for compounds of the "amphi" salt type to exist to an appreciable extent in aqueous solution. Such an objection cannot be raised if the compounds are regarded as "molecular" compounds with the metallic atom co-ordinated with the oxygen of the carboxyl group or with the nitrogen of the amino-group (Pfeiffer, *loc. cit.*). The observed regularities in the effects of barium, calcium, and sodium haloids make it appear probable that the influence of salts on the rotatory powers of hydroxy- and amino-compounds is due to the same cause. It may therefore be assumed that this influence is due to combination of the salts with the optically active compounds in question, the latter reacting with the salts in consequence of the residual affinity of the oxygen and nitrogen atoms in the alkylic

hydroxyl and amidogen radicles respectively. It is thus no longer necessary to explain the alterations in rotatory power caused by the presence of neutral salts by means of the recently revived hypothesis of Arndtsen that the changes in rotatory power are due to a displacement in the equilibrium of hypothetical isodynamic forms of the active compound.

An examination of table X shows that there are certain regularities in the rotatory powers of the derivatives from the optically active α -amino-acids. The rotatory powers of the hydrochlorides of those varieties of the active amino-acids in this table are in every case more positive than those of the amino-acids in aqueous solution, and in general the molecular rotations of the potassium salts of the benzoylamino-acids are more positive than those of the hydrochlorides of the amino-acids. The aminoacylglycines possess relatively high positive rotations in aqueous solution, whilst the glyceryl derivatives of the amino-acids in question are usually levorotatory, glyceryl-*L*-phenylalanine being a noticeable exception. Similar regularities are observable in the recorded values for the diketopiperazines, β -naphthalenesulphonyl, and *N*-methyl derivatives of the same amino-acids.

Fischer and Raske (*Ber.*, 1907, 40, 3717) have transformed *L*-serine into *L*- β -chloro- α -aminopropionic acid, and the latter into *d*-alanine, without displacing groups directly attached to the asymmetric carbon atom, and they have pointed out that the hydrochlorides of these amino-acids possess more positive rotatory powers than the configuratively related parent acids. A similar regularity is evident in the rotatory powers of the related compounds *L*-asparagine and *L*-aspartic acid, and the author maintains that the rotatory values for the amino-acids and their derivatives in table X indicate that all these compounds possess the same relative configurations. The influence of temperature on the rotatory powers of *L*-asparagine, *L*-aspartic acid (T., 1915, 107, 1509), and *d*-glutamic acid is similar to that on *d*-alanine in aqueous solution, and the rotatory powers of these compounds are increased by the addition of sodium or barium haloids. The similarity between *L*-aspartic acid and *d*-glutamic acid is shown admirably by the curves of Andrlík (*Zeitsch. Ver. deut. Zuckerind.*, 1903, 948) and Wood (T., 1914, 105, 1988) illustrating the effect of varying amounts of bases on the rotations of these acids. It should also be pointed out that those amino-acids which have been obtained from protein occur in the optically active varieties denoted in table X. Moreover, Ehrlich observed that when certain inactive amino-acids were subjected to the action of yeast in sugar solutions, the forms which survived attack were the enantiomorphs of the naturally occurring

TABLE X.

The Optical Rotatory Powers $[\alpha]_D^{20}$ of α -Amino-acids and of certain Derivatives from them.

Amino-acid.	Hydro- chloric acid.	Water.	Benzylamino-acid (in KOH,aq.).	Aminoseylglycine (in water).	Glycylamino- acid (in water).	Hydantoin.* + 50.6° (water)
<i>D</i> -Alanine ¹	+ 2.7°	+ 14.3°	+ 36.5°	+ 50.2°	— 50.0°	—
<i>L</i> -Serine ²	— 6.8	+ 14.4	+ 43.6 (in NaOH,aq.) (<i>p</i> -nitrobenzoyl)	—	—	—
<i>L</i> - β -Chloro- α -aminopropionic acid ³	— 15.5	+ 0.9	—	—	—	—
<i>D</i> - α -Aminobutyric acid ⁴	+ 8.0	+ 19.6	+ 30.7 (in NaOH,aq.)	+ 86.4 (K) + 26.8 (A & C) + 90	— 20.3	—
<i>D</i> -Valine ⁵	+ 6.4	+ 28.7	—	—	— 19.7	— 97.5 (phenyl- hydantoin in alcohol).
<i>D</i> - α -Aminohexonic acid ⁶	—	+ 23.0	+ 21.9	—	—	—
<i>L</i> -Leucine ⁷	— 10.3	+ 15.6	+ 6.6 (in NaOH,aq.)	+ 85.5	— 35.0	— 68.2 (in NaOH,aq.)

* Hydantoins, Dakin & Dudley, *J. Biol. Chem.*, 1913, 17, 29; 1914, 18, 48; T., 1915, 107, 434.¹ Fischer, *Ber.*, 1906, 39, 2914; 1906, 39, 453; 1907, 40, 943.² Fischer and Jacobs, *Ber.*, 1906, 39, 2942; Fischer and Haske, *Ber.*, 1907, 40, 3717.³ Fischer and Haske, *loc. cit.*⁴ Fischer and Mounsey, *Ber.*, 1900, 33, 2383; Koelker, *Zeitsch. physiol. Chem.*, 1911, 73, 312; Abderhalden and Chang, *ibid.*, 1912, 77, 471.⁵ Fischer, *Ber.*, 1906, 39, 2320; Fischer and Scheibler, *Annalen*, 1908, 363, 136.⁶ Fischer and Hagenbach, *Ber.*, 1901, 34, 3764.⁷ Fischer, *Ber.*, 1900, 33, 2370; *Ber.*, 1906, 39, 2893; Fischer and Steingroover, *Annalen*, 1908, 365, 167.

TABLE X.—(continued).

 The Optical Rotatory Powers ($[\alpha]_D^{20}$) of α -Amino-acids and of certain Derivatives from them.

Amino-acid.	Hydro- chloric acid.	Benzoylamino-acid (in KOH,aq.).	Aminocoryglycine (in water).	Glycylamino- acid (in water).	Hydantoin.*
<i>d</i> -isoLeucine ⁸	+ 11.3° + 40.6°	(in NaOH,aq.)	+ 33.6°	— 14.7°	—
<i>L</i> -Asparagine ⁹	— 4.9 + 28.5	—	—	— 6.4	—
<i>L</i> -Aspartic acid ¹⁰	+ 4.3 + 25.7	+ 37.4	—	+ 11.1	— 125 (in NaOH,aq.).
<i>d</i> -Glutamic acid ¹¹	+ 9.9 + 30.8	+ 18.7	—	— 6.3	— 79 (in NaOH,aq.)
<i>L</i> -Phenylalanine ¹²	— 35.3 — 7.1	+ 17.1	+ 54.2	+ 41.4	— 96.4 (in 50 per cent. alcohol).
<i>L</i> -Tyrosine ¹³	— — 8.6	+ 19.2	—	—	— 143 (in NaOH,aq.)

 * Hydantoins, Dakin and Dudley, *J. Biol. Chem.*, 1913, 17, 29; 1914, 18, 48; T., 1915, 107, 434.

⁸ Lacquin, *Bull. Soc. chim.*, 1907 [iv], 1, 595; Abderhalden, Hirsch, and Schuler, *Ber.*, 1906, 42, 3394.

⁹ Fischer and Koenigs, *Ber.*, 1904, 37, 4586.

¹⁰ Fischer, *Ber.*, 1899, 32, 2461; Fischer and Fiedler, *Annalen*, 1910, 375, 181.

¹¹ Fischer, Kropf, and Stahlmeidt, *Annalen*, 1909, 365, 189.

¹² Fischer and Mounseyrat, *loc. cit.*; Fischer and Schoeller, *Annalen*, 1907, 357, 1.

¹³ Fischer, *Ber.*, 1899, 32, 3638.

forms. The configurations of the constituent amino-acids also appear to condition the hydrolysis of polypeptides by enzymes; thus only those compounds containing the naturally occurring optically active forms of the amino-acids are hydrolysed by trypsin (Fischer and Abderhalden, *Zeitsch. physiol. Chem.*, 1907, 51, 264). The optically active amino-acids appearing in table X may therefore be conveniently termed the "l"-aliphatic α -amino-acids.

It may be recalled that *l*-phenylaminoacetic acid was obtained by Ehrlich by the action of yeast on the optically inactive amino-acid. The rotatory values for this acid recorded by Fischer and Weichhold (*Ber.*, 1908, 41, 1293) are $[\alpha]_D^{20} -112.6^\circ$ (water), -158° (*N*-hydrochloric acid), and -260° for the formyl derivative, values which may be compared with those for *l*-phenylalanine, $[\alpha]_D^{20} -35.3^\circ$ (water), -7.1° (hydrochloric acid), and $+75.2^\circ$ for the formyl compound. These results appear to show that *d*-phenylaminoacetic acid is related configuratively to the active amino-acids in table X.

The α -Halogen Acids.

The optically active halogen acids may be obtained from the active hydroxy-acids by phosphorus haloids or thionyl chloride, from the active amino-acids by nitrosyl chloride (or bromide), or by the resolution of the inactive compounds. The racemisation which usually accompanies reactions involving the displacement of groups attached to the asymmetric carbon atom and the reactivity of the halogen towards bases, frequently make it difficult to obtain the active forms of the halogen acids in a state of purity. There are necessarily fewer derivatives of the halogen acids than of the hydroxy- or amino-acids, and there is no doubt that some of the values given in the literature for halogen acids and derivatives from them are numerically lower than those for the pure active compounds. The values in table XI for certain *d*- α -halogen acids indicate the great probability that all these compounds possess the same configurations. Inasmuch as these optically active halogen acids are all dextrorotatory, their usual designation *d*- may also be used to indicate their configurative similarity to one another (see footnote, p. 547).

The rotatory powers of the esters of the *d*- α -halogen-propionic and -succinic acids diminish with increase of molecular weight, and it appears from the table that the glycines possess higher molecular rotatory powers than the parent acids. The specific rotatory power of *d*-bromopropionic acid diminishes with rise of temperature (Ramberg), as is also the case for methyl and ethyl *d*- α -chloropropionates (J. W. Walker) and for methyl *d*-bromosuccinate

TABLE XL.
The Specific Rotations ($[\alpha]_D^{25}$) of certain d- α -Halogen Acids and their Derivatives.

	Acid.	Methyl ester.	Ethyl ester.	Propyl ester.	Bromoacetyl-glycine.	References.
<i>d</i> - α -Chloropropionic acid	+ 14*	+ 26.8* (at 5°)	+ 19.9 (at 5°)	+ 11.0* (at 6°)	—	Frankland and Garner, T., 1914, 105, 1101; J. W. Walker, T., 1896, 67, 918.
<i>d</i> - α -Bromopropionic acid	+ 29.0	+ 42.6	+ 35.5	+ 22	+ 35.3 (water)	J. W. Walker, loc. cit., Ramberg, <i>Annalen</i> , 1909, 370, 234; Fischer, <i>Ber.</i> , 1907, 40, 489.
<i>d</i> - α -Bromoisovaleric acid	+ 9.0 (water); 22.8 (benzene)	—	—	—	+ 47.5 (alcohol)	Fischer and Scheibler, <i>Ber.</i> , 1908, 41, 889, 2891.
<i>d</i> - α -Bromosuccinic acid	+ 49.4	—	+ 50	—	+ 62 (alcohol)	Fischer and Carl, <i>Ber.</i> , 1906, 39, 3998.
<i>d</i> - α -Bromo- β -methylvaleric acid	+ 26.5 (benzene)	—	—	—	+ 64.4 (alcohol)	Abderhalden, Hirsch, and Schuler, <i>Ber.</i> , 1909, 42, 3394.
<i>d</i> - α -Bromo- β -phenylpropionic acid	+ 10.4	—	+ 9	—	+ 14.6 (alcohol)	Senter, Drew, and Martin, this vol., p. 158; Fischer and Carl, loc. cit.; Fischer and Schoeller, <i>Annalen</i> , 1907, 357, 1.
<i>d</i> -Chlorosuccinic acid	+ 21.7 (water); 55.7 (ethyl acetate)	+ 42.3	+ 32.7	+ 25	—	Walden, <i>Ber.</i> , 1898, 29, 1689; McKenzie and Barrow, T., 1911, 99, 1919.
<i>d</i> -Bromosuccinic acid	+ 41.8 (water); 76.5 (ethyl acetate)	+ 51.2	+ 41.0	+ 38.0	—	Walden, <i>Ber.</i> , 1895, 28, 1290, 17, 264; <i>Zeitsch. physikal. chem.</i> , 1895, 17, 264.
<i>d</i> -Dichlorosuccinic acid	+ 80.4 (ethyl acetate)	—	+ 66 (chloroform)	—	—	Holmberg, <i>Svensk. Kem. Tid.</i> , 1912; Darzens and Séjourné, <i>Compt. rend.</i> , 1912, 154, 1616.
<i>d</i> -Dibromosuccinic acid	+ 70 (water)*; 148 (ethyl acetate)	—	—	—	—	Holmberg, <i>Svensk. Kem. Tid.</i> , 1911; McKenzie, T., 1912, 101, 1198.

* Approximate values by calculation.

(Walden). On the other hand, Senter, Drew, and Martin find that the levorotatory power of *l*- α -bromo- β -phenylpropionic acid is increased by rise of temperature.

It has been shown by Frankland and Turnbull (*loc. cit.*) that the optically active methyl $\alpha\beta$ -dichloropropionate obtained by the action of phosphorus pentachloride on methyl *d*-glycerate is dextrorotatory, whereas the higher esters are levorotatory. It would thus seem that these esters are related to the *d*-halogen acids in table XI, the temperature coefficients of the esters in question being similar in character to that of *d*- α -bromo- β -phenylpropionic acid. The rotations of the *d*-phenylhalogenacetic acids are considerably higher in benzene solution than in aqueous solution, and the specific rotation of the ethyl ester appears to be lower than that of the free acid (McKenzie and Barrow, T., 1911, **99**, 1919); moreover, the rotatory powers of the methyl and ethyl esters diminish with rise of temperature (J. W. Walker). These facts indicate that the dextrorotatory acids are configuratively related to *d*-chloropropionic acid.

The Relationship between the Optically Active α -Halogen Acids and α -Amino-acids.

The foregoing considerations render it possible to determine whether the conversions of the optically active α -amino-acids into the halogen acids which have been effected by nitrosyl haloids are or are not similar in stereochemical character. It has often been assumed that the action of nitrosyl haloids on the active amino-acids is always of the same character, but it is certain that a given reagent does not invariably act in the same way on compounds of similar type. The following conclusions may be drawn from the relationships which have been established for the active α -amino-acids and α -bromo-acids respectively:

(a) The transformations *d*-alanine \rightarrow *l*-bromopropionic acid, *l*-aspartic acid \rightarrow *l*-chlorosuccinic acid (or *l*-bromosuccinic acid), *d*-valine \rightarrow *l*- α -bromoisovaleric acid, *l*-leucine \rightarrow *l*- α -bromoisohectic acid, *d*-isoleucine \rightarrow *l*- α -bromo- β -methylvaleric acid, and *l*-phenylalanine \rightarrow *l*- α -bromo- β -phenylpropionic acid (by the action of nitrosyl haloids), are all of the same stereochemical character, that is to say, they are either all "normal" or all "abnormal" reactions. Inasmuch as *d*-glutamic acid and *d*- α -aminobutyric acid are, according to the author, related to the above amino-acids, it is almost certain that the changes *d*-glutamic acid \rightarrow *l*- α -chloroglutaric acid ($[\alpha]_D^{25} - 12.5^\circ$ in water) and *l*- α -aminobutyric acid \rightarrow *d*- α -bromobutyric acid ($[\alpha]_D + 15.4^\circ$, Abderhalden and Chang, *loc.*

cit.) are also of this type (for references, see Frankland, T., 1913, 103, 728).

(b) The action of nitrosyl bromide on esters of *d*-alanine, *L*-aspartic acid, *L*-leucine, and *L*-phenylalanine is opposite in character to that of this reagent on the amino-acids mentioned in paragraph (a).

(c) The action of ammonia on *L*- α -bromopropionic acid (or ester), *L*-bromosuccinic acid, *L*- α -bromo*isovaleric* acid, *L*- α -bromo*isohexic* acid (or ester), *L*- α -bromobutyric acid or *L*- α -bromo- β -phenylpropionic acid is opposite to that of nitrosyl bromide on the amino-acids mentioned in paragraph (a). Fischer has shown that the action of potassium phthalimide on ethyl *L*- α -bromopropionate (*Ber.*, 1907, 40, 489), that of trimethylamine on *d*- α -bromopropionic acid (*Ber.*, 1907, 40, 5000), and that of methylamine on *L*- α -bromopropionic acid, *d*- α -bromo*isohexic* acid, or *d*- α -bromo- β -phenylpropionic acid, all take place in the same stereochemical sense as the action of ammonia on the same compounds (Fischer and von Mechel, *Ber.*, 1916, 49, 1355). It is exceedingly probable that the numerous examples of the action of ammonia on the active α -bromoacyl derivatives of amino-acids which have been investigated by Fischer and Abderhalden are all of this type.

(d) The action of ammonia on *L*- α -bromo*isovaleric* acid or on *L*- α -bromo- β -methylvaleric acid is the reverse of that of the same reagent in the examples given in paragraph (c).

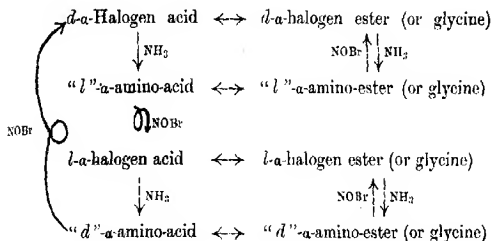
In order to decide in which of the above reactions a change of configuration takes place, it becomes necessary to ascertain whether the active α -amino-acids in table X possess the same relative configurations as the *d*-halogen acids in table XI. Although these two classes of compounds can scarcely be considered to be "similarly constituted," it is desirable that a comparison of the rotatory powers of their derivatives should be made in this connexion. Unfortunately, there are very few similar classes of derivatives of the amino-acids on the one hand and of the halogen acids on the other the rotatory powers of which are available for a comparative study of these compounds. The most complete series of derivatives are the α -bromoacyl- and the α -aminoacyl-amino-acids. It is evident from table XII that there is a close relationship between the values for the aminoacyl derivatives and the bromoacyl derivatives from which they are obtained, and it appears to the author that this relationship indicates the great probability that the amino-derivatives are configuratively related to the bromo-derivatives in question. For example, *d*- α -bromopropionyl-*L*-alanine ($[\alpha]_D + 68.2$) is related to *d*-alanyl-*L*-alanine ($[\alpha]_D + 68.9$), and not to *L*-alanyl-*L*-alanine ($[\alpha]_D + 21.6$). If, for the purpose of this

TABLE XII.
The Optical Rotatory Powers ($[\alpha]_D^{25}$) of certain α -Bromoacyl and α -Aminoacyl Derivatives of the α -Amino-acids.

Amino-acid. Glycine	Amino- acid.	Chloro- acetyl- amino- acid.	Glycyl- amino- acid.	<i>d</i> - α -Bromo- propionyl- amino- acid. + 38.3°	<i>d</i> -Alanyl- amino- acid. + 50.2°	<i>d</i> - α -Bromo- isohexoylamino- acid. + 62.0° (in alcohol)	<i>d</i> -Leucylamino- acid + 86.0°	References.
<i>d</i> -Alanine	+ 2.7°	- 45°	- 50°	- 16.5	- 21.6	+ 23.3 (in alcohol)	+ 23.5 (in methyl alcohol)	Fischer, <i>Ber.</i> , 1908, 41. 850; 1906, 39, 2911.
<i>L</i> -Alanine	- 2.7	+ 45	+ 50	+ 68.2	+ 68.9	—	—	Fischer, <i>Ber.</i> , 1906, 39, 453; Fischer and Schulze, <i>Ber.</i> , 1907, 40, 943.
<i>L</i> -Leucine	- 10.3	- 13.8	- 35.2 (in alcohol)	+ 2.0	- 17.0	+ 16.2 (in ethyl acetate)	- 13.4 (in <i>N</i> -NaOH)	Fischer and Reake, <i>Ber.</i> , 1906, 39, 3989.
<i>d</i> -Leucine	+ 10.3	+ 13.8	+ 35.2	—	—	+ 35 (in ethyl acetate)	+ 68.9 (in <i>N</i> -HCl)	Fischer, <i>Ber.</i> , 1907, 40. 1754.
<i>d</i> -isoLeucine ...	+ 10.5	+ 25.0 (in alcohol)	- 14.7	+ 24.5 (in alcohol)	+ 6.1 (in HCl)	+ 49 (in ethyl acetate)	+ 18.1	Fischer and Koelker, <i>An- nalen</i> , 1907, 384, 39.
<i>L</i> -isoLeucine ...	- 10.5	- 25.0 (in alcohol)	+ 14.7	—	—	+ 19 (in alcohol)	+ 53.1	Aberghalden, Hirsch, and Schuler, <i>Ber.</i> , 1909, 42, 3994.
								Aberghalden and Schuler, <i>Ber.</i> , 1910, 43, 907.

The values in this table are for the specific rotations in aqueous solution unless stated otherwise.

discussion, the active amino-acids in table X be denoted by the designation "l," it follows that the "l" amino-acids possess the same configuration as the *d*-halogen acids,* and that the action of ammonia on the above halogen acids (with the exception of α -bromo-*isovaleric* acid and α -bromo- β -methylvaleric acid) or their derivatives does not cause a configurative change. It may be mentioned in this connexion that Scheibler has conclusively shown that the action of ammonia on *l*- $\beta\beta'$ -iminodibutyric acid, yielding *l*- β -aminobutyric acid, is a "normal" action (*Ber.*, 1912, 45, 2272). The transformations of the aliphatic α -amino-acids (including phenylalanine), with the exception of valine and *isoleucine*, may be represented by the following scheme (compare Frankland, T., 1913, 103, 741):



The scheme for "l"-valine and "l"-*isoleucine* is similar, except that the action of ammonia on the free bromo-acids is assumed to be "abnormal." *isoleucine* contains two asymmetric carbon atoms, and a true Walden inversion cannot be effected, but the transformations involved are similar to those for valine.

The Relationship between the Optically Active α -Amino- and α -Hydroxy-acids.

It is clear from the relationships which have been established for the amino-acids and hydroxy-acids, respectively, that the trans-

* It appears advisable to retain for the present the designation *d*- for the dextrorotatory α -halogen acids to denote their configurative similarity to one another. If the above view that these dextrorotatory α -halogen acids are related configuratively to the "l"- α -amino-acids is correct, it would be preferable to indicate their configurations by the prefix "L." It may be mentioned here that it is not possible to denote the relative configuration of a given optically active compound (containing only one asymmetric carbon atom) always by means of the same prefix (Clough, P., 1913, 29, 359).

formations (effected by nitrous acid) *d*-alanine \rightarrow *d*-lactic acid, *l*-serine \rightarrow *d*-glyceric acid, *d*-valine \rightarrow *d*- α -hydroxyisovaleric acid, *l*-leucine \rightarrow *l*- α -hydroxyisohexoic acid, *l*-aspartic acid \rightarrow *l*-malic acid, *d*-glutamic acid \rightarrow *l*- α -hydroxyglutaric acid, and *l*-phenylalanine \rightarrow *l*- β -phenyl-lactic acid (Clough, unpublished) are all of the same stereochemical type. It is not possible with the data at present available to make a satisfactory comparison of the rotatory powers of the active hydroxy-acids with those of the active amino-acids. The rotatory powers of very few α -amino-esters have been determined, and of only two hydroxyacylglycines. There are, however, certain similarities which seem to indicate that the "*l*"- α -amino-acids possess the same relative configurations as the "*l*"-hydroxy-acids (which are enantiomorphously related to *d*-tartaric acid).

The dextrorotatory powers of "*l*"-lactic acid and "*l*"-glyceric acid in aqueous solution are reversed and the levorotatory power of *l*-malic acid is increased on raising the temperature; the dextrorotatory powers of "*l*"-alanine and *l*-aspartic acid are reversed and that of "*l*"-glutamic acid is diminished with rise of temperature. Moreover, the changes in the rotatory powers of "*l*"-alanine, *l*-asparagine, *l*-aspartic acid (or ester), "*l*"-glutamic acid, "*l*"-lactic acid (or ester), and *l*-malic acid (or ester) caused by inorganic haloids in aqueous solution are all in the same sense. It is therefore suggested that the action of nitrous acid on the active aliphatic α -amino-acids is a "normal" action.

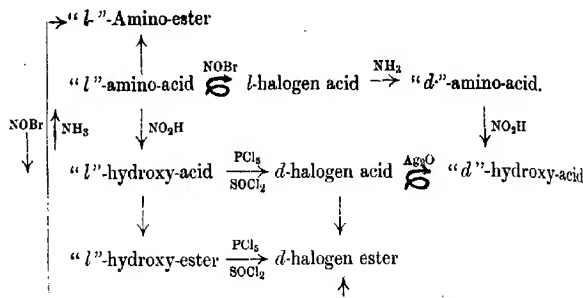
The Relationship between the Optically Active α -Hydroxy- and α -Halogen Acids.

The conclusions that have been drawn regarding the configurative relationships of the hydroxy-acids on the one hand and of the halogen acids on the other make it appear almost certain that the conversions of "*l*"-lactic acid (or ester) by phosphorus haloids or thionyl chloride into *d*-halogen-propionic acids (or esters), *l*-malic acid (or esters) by phosphorus pentachloride or thionyl chloride into *d*-chlorosuccinic acid (or esters), ethyl *l*- α -hydroxyisohexoate by phosphorus and bromine into ethyl *d*- α -bromoisohexoate, and of ethyl *d*-tartrate by thionyl chloride into ethyl *l*-dichlorosuccinate, are reactions of the same stereochemical character. When it is remembered that the specific rotatory powers of the *d*-halogen esters diminish as the homologous series are ascended, and that the rotatory powers of the *d*-bromo-esters are more positive than those of the corresponding chloro-esters, if

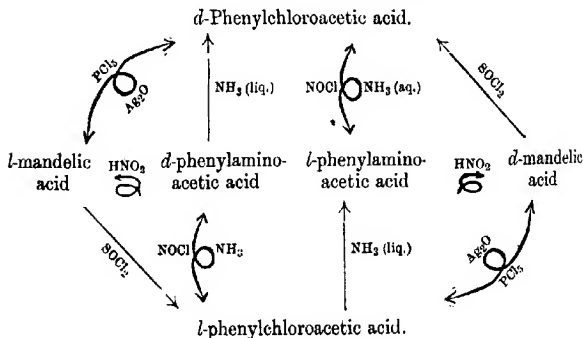
is not surprising that the levorotatory esters of "*l*"-glyceric acid yield, on treatment with phosphorus pentachloride, esters of $\alpha\beta$ -dichloropropionic acid diminishing in rotatory power from a positive value for the methyl ester to negative values for the higher esters, and that *isobutyl l*- α -hydroxybutyrate yields a levorotatory chloro-ester but a dextrorotatory bromo-ester, these halogen esters being derived, presumably, from α -chloro- and α -bromo-butyric acids possessing the same configurations as *d*-chloropropionic acid (Guye and Jordan, *Bull. Soc. chim.*, 1896, [iii], 15, 495). It appears probable that the relationship between the optically active aliphatic normal secondary alcohols and the halogen compounds prepared from them by hydrogen haloids, and that between *l*- β -hydroxybutyric acid (or ester) and *d*- β -chlorobutyric acid (or ester) obtained from it by phosphorus pentachloride, are also of the same character. There is little doubt that thionyl chloride would react with these hydroxy-compounds in the same manner as hydrogen haloids or phosphorus pentachloride respectively.

If it is assumed that the "*l*"-amino-acids are related to the *d*-halogen acids and also to the "*l*"-hydroxy-acids, it follows that the "*l*"-hydroxy-acids are of the same configuration as the *d*-halogen acids. It may be recalled that the temperature-rotation curves for ethyl *d*-bromopropionate and ethyl *d*-bromosuccinate are similar in character to those of *d*-("*l*")lactic acid (or ester) and *l*-malic acid (or ester). On the other hand, the influence of temperature on methyl *d*- $\alpha\beta$ -dichloropropionate is opposite to that on methyl "*l*"-glycerate, from which it is prepared.

The fact that the rotatory powers of the *d*-halogen esters diminish as the carbalkyloxy-groups increase, whilst the rotations of the *d*-hydroxy-esters increase as the series is ascended (at least for the early members), is in accordance with the above view. It may therefore be assumed that the action of phosphorus haloids and of thionyl chloride on the aliphatic α -hydroxy-acids (or esters) which have been investigated is not accompanied by a change of configuration. The following scheme would then include most of the changes which have so far been realised with α -derivatives of propionic acid, butyric acid, succinic acid, *isohexic* acid, and (with the possible exception of the action of thionyl chloride) β -phenylpropionic acid:



It has been suggested above that *l*-mandelic acid is configuratively allied to *d*-malic acid, that the *l*-phenyl-halogen-acetic acids are related to *l*-chlorosuccinic acid, and that *l*-phenylaminoacetic acid has a similar configuration to that of *d*-aspartic acid. Inasmuch as it has been assumed that *l*-chlorosuccinic acid is configuratively related to *d*-malic acid and to *d*-aspartic acid, it would follow that *l*-mandelic acid, the *l*-phenyl-halogen-acetic acids, and *l*-phenylaminoacetic acid all possess the same relative configurations. In any case, it is almost certain from the rotatory powers of the latter compounds that their common designation (*l*-) may also be used to imply a similar configurative relationship. The following scheme, then, represents most of the transformations of the derivatives of phenylacetic acid, and also (as far as they have been studied) those of the β -derivatives of β -phenylpropionic acid and of the α -derivatives of α -phenylpropionic acid, with the exception of those reactions of the latter in which complete racemisation occurs. The reactions which have been effected with esters of the acids are likewise in conformity with this scheme.



Summary of Conclusions.

(a) A comparison of the optical rotatory powers of the acids commonly written *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid (which possess the same relative configurations), and of derivatives from them, has led the author to assume that the optical rotatory powers of similarly constituted compounds possessing the same configuration are, in general, influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom.

(b) The rotatory powers of the above four acids, and also of *d*- α -hydroxybutyric acid, *l*- α -hydroxyisovaleric acid, *d*- α -hydroxyisohexic acid, *d*- α -hydroxy- β -phenylpropionic acid, *d*- α -hydroxyglutaric acid and their derivatives, indicate that all these acids possess the same relative configurations. For the sake of convenience, the designation "*d*" has been used to denote the configurations of these compounds.

(c) Similarly, it is assumed that the naturally occurring α -amino acids, commonly denoted as *d*-alanine, *l*-serine, *l*-aspartic acid, *d*-valine, *l*-leucine, *d*-isoleucine, *d*- α -aminobutyric acid, *d*-glutamic acid, *l*-phenylalanine, and *l*-tyrosine, all possess the same configurations. The configurations of these compounds have been denoted by the symbol "*l*."

(d) The dextrorotatory (*d*-) α -halogen acids which have been isolated are assumed to be configuratively similar compounds.

(e) A comparison of the rotatory powers of the optically active α -bromoacyl-amino-acids with those of the α -aminoacyl-amino-acids leads to the view that the amino-acids mentioned in paragraph (c) are related configuratively to the halogen acids mentioned in paragraph (d).

(f) It is suggested that the "*d*"-hydroxy-acids are enantiomorphously related to the "*l*"-amino-acids, and therefore to the *d*-halogen acids.

(g) The levorotatory compounds, *l*-mandelic acid, *l*-phenylchloroacetic acid, and *l*-phenylaminoacetic acid, are assumed to possess the same configurations.

*Experimental Data.**l*-Lactic Acid.

The aqueous lactic acid was obtained by the hydrolysis of methyl *l*-lactate by boiling with ten times its weight of water for six

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hours, and subsequent distillation of the methyl alcohol. This specimen contained 92 per cent. of *l*-lactic acid, and 8 per cent. of *d*-lactic acid.

$$p=10.73.$$

<i>t</i>	15°.	18°.	36°.	52°.	62°.	70°.	15°.
<i>d</i>	1.03	1.03	1.02	1.01	1.01	1.00	1.03
α_D^t (<i>l</i> = 4) ...	-0.95°	-0.88°	-0.32°	$\pm 0.00^\circ$	+0.18°	-0.30°	-0.95°
$[\alpha]_{D,4}^t$	-2.2°	-2.0°	-0.7°	$\pm 0.0^\circ$	+0.4°	+0.7°	-2.2°

A specimen of *l*-lactic acid prepared from zinc *l*-lactate showed similar behaviour.

Methyl l-Lactate.

This ester was prepared from zinc *l*-lactate, obtained from a dextrorotatory lactic acid syrup, which gave $\alpha_D(l=1) + 5.2$, by Patterson and Forsyth's method (T., 1913, 103, 2263). The specimen contained about 5 per cent. of methyl *d*-lactate.

	<i>d</i> .	α_D^t (<i>l</i> = 1).	α_{gr}^t .	α_{vi}^t .	$[\alpha]_D^t$.	$[\alpha]_{gr}^t$.	$[\alpha]_{vi}^t$.*
15°	1.097	+7.96°	+9.05°	+11.95°	+7.26°	+8.25°	+10.89°
20	1.093	+8.15	9.17	12.25	7.46	8.39	11.21

* The rotations recorded in this paper and in the previous paper (*loc. cit.*) for mercury violet light ($[\alpha]_{vi}$) are for $\lambda = 4078$.

Methyl l-Lactate in Water.

<i>p</i> .	<i>d</i> ²⁰ .	α_D^{20} (<i>l</i> = 1).	α_{gr}^{20} .	α_{vi}^{20} .	$[\alpha]_D^{20}$.	$[\alpha]_{gr}^{20}$.	$[\alpha]_{vi}^{20}$.
100	1.093	+8.15°	+9.17°	+12.25°	+7.46°	+8.39°	+11.21°
80.0	1.086	3.60	3.81	3.90	4.1	4.4	4.5
50.0	1.063	1.16	1.34	0.54	2.1	2.5	1.0
20.0	1.026	0.72 (<i>l</i> = 2)	0.73	-0.08	1.8	1.8	-0.2
10.0	1.012	0.27 (<i>l</i> = 2)	0.20	-0.10	1.3	1.4	-0.5
5.36	1.005	0.28 (<i>l</i> = 4)	0.30	-0.30	1.3	1.4	-0.9

d-Alanine in Water.

The specimen employed was prepared from silk by Fischer's method (*Ber.*, 1906, 39, 462).

$$p=5.85.$$

<i>t</i>	13°.	16°.	29°.	40°.	64°.	74°.	80°.
<i>d</i>	1.02	1.02	1.01	1.01	1.00	1.00	1.00
α_D^t (<i>l</i> = 4) ...	+0.74°	0.68°	0.56°	0.40°	0.04°	-0.04°	-0.15°
$[\alpha]_{D,4}^t$	+3.1°	2.9°	2.4°	1.7°	0.2°	-0.2°	-0.5°

$$p=9.81.$$

<i>t</i>	15°.	20°.	30°.	45°.	60°.	72°.
<i>d</i>	1.03	1.03	1.03	1.02	1.02	1.01
α_D^t (<i>l</i> = 4)	+1.41°	1.32°	1.10°	0.77°	0.48°	0.29°
$[\alpha]_{D,4}^t$	+3.5°	3.3°	2.7°	1.9°	1.2°	0.7°

D-Alanine in Aqueous Sodium Hydroxide (1 mol.).

$$p = 7.79, d^{15} 1.045, a_{gr}^{15} (l=2) + 1.06^\circ, [a]_{gr}^{15} + 6.5^\circ.$$

$$p = 1.61, d^{15} 1.01, a_{gr}^{15} (l=4) + 0.38^\circ, [a]_{gr}^{15} + 5.8^\circ.$$

D-Alanine in Hydrochloric Acid.

$$p = 8.098 \text{ (1 mol. HCl)}; d^{15} 1.036, a_{gr}^{15} (l=2) + 2.40^\circ, a_{gr}^{15} + 2.88^\circ, [a]_D^{15} + 14.3^\circ, [a]_{gr}^{15} + 17.1^\circ.$$

$$p = 5.605 \text{ (1.5 mols. HCl)}; d^{15} 1.033, a_D^{15} (l=2) + 1.70^\circ, a_{gr}^{15} + 2.06^\circ, [a]_D^{15} + 14.7^\circ, [a]_{gr}^{15} + 17.8^\circ.$$

Ethyl L-Aspartate.

This ester was prepared by Fischer's method (*Ber.*, 1901, **34**, 452).

$$d^{20} 1.085, a_D^{20} (l=0.5), -5.39^\circ, a_{gr}^{20} - 5.60^\circ, a_{gr}^{20} - 6.36^\circ, a_{gr}^{20} - 13.33^\circ, [a]_D^{20} - 9.93^\circ, [a]_{gr}^{20} - 10.32^\circ, [a]_{gr}^{20} - 11.72^\circ, [a]_{gr}^{20} - 24.57^\circ.$$

D-Glutamic Acid.

Water; $p = 0.99$.

t	d^t .	$a'_b (l=4)$.	a'_{gr} .	$[a]_b^t$.	$[a]_{gr}^t$.
15°	1.004	+ 0.41°	+ 0.52°	+ 10.3°	+ 13.1°
40	0.995	0.32	0.43	8.1	10.9
51	0.992	0.29	0.40	7.4	10.2
60	0.998	0.27	0.37	6.9	9.5
25*	—	—	—	9.4	12.4

* Interpolated.

$p = 1.50$.

25°	1.003	0.66	0.80	11.0	13.3
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$p = 2.91$.

44°	1.002	1.20	1.44	10.3	12.3
64	0.994	1.00	1.25	8.6	10.8
75	0.990	0.90	1.15	7.8	10.0
25	—	—	—	11.7	14.0

Hydrochloric acid (N), 1.5 mols.; $p = 8.752$.

t	d^t .	$a'_b (l=2)$.	a'_{gr} .	a'_{vi} .	$[a]_b^t$.	$[a]_{gr}^t$.	$[a]_{vi}^t$.
13°	1.048	+ 5.81°	7.05°	15.60°	31.7°	38.4°	85.1°
32	1.042	5.50	6.72	14.65	30.2	36.8	80.3
43	1.037	5.32	6.53	14.10	29.3	36.0	77.7
25	—	—	—	—	30.7	37.4	82.1

Aqueous sodium hydroxide (1 mol.).

$$p = 21.2, [\alpha]_{D}^{25} - 0.8^{\circ}; p = 12.25, [\alpha]_{D}^{25} - 3.6^{\circ}; p = 2.86, [\alpha]_{D}^{25} - 6.1^{\circ}.$$

Aqueous sodium hydroxide (2 mols.).

$$p = 6.56, [\alpha]_{D}^{25} + 11.7^{\circ}; p = 1.44, [\alpha]_{D}^{25} + 10.2^{\circ}; [\alpha]_{D}^{40} + 8.6^{\circ}.$$

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant towards the expense of this investigation, and to Dr. J. K. Wood for a supply of synthetic alanine from which the active benzoylalanine was prepared. The experimental portion of this work was performed at Birkbeck College, London.

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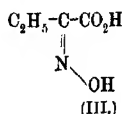
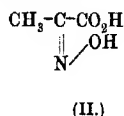
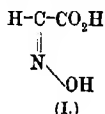
[Received, March 25th, 1918.]

XLV.—*The Dissociation Constants of some Higher Members of the α -Oximino-fatty Acids.*

By CEDRIC STANTON HICKS.

HANTZSCH and Miolati (*Zeitsch. physikal. Chem.*, 1892, **10**, 1), in an investigation of the dissociation constants of the lower members of the α -oximino-fatty acids, drew the conclusion that in the series $C_nH_{2n+1} \cdot C(:NOH) \cdot CO_2H$ as the series is ascended the dissociation constant diminishes in value, not steadily, but by a series of oscillations. Thus it was found that K for the first four acids, in which a hydrogen atom is successively displaced by the methyl, ethyl, and propyl groups, varied as follows: 0.0995, 0.0514, 0.0530, and 0.0685.

They considered that the variations were due to alternate fluctuations in the proximity of the hydroxyl to the carboxyl group, nearness of the hydroxyl, according to them, weakening the acid. This may be expressed graphically thus:



As pointed out by Inglis and Knight (T., 1908, **93**, 1595), if the value for the second acid is abnormal, the series loses its interest,

and they accordingly began a reinvestigation of the conductivities of these acids.

In continuation of the work begun by these authors, an investigation of the dissociation constants of the higher members of the series has been undertaken.

EXPERIMENTAL.

The acids were prepared by Bouveault and Locquin's method (*Bull. Soc. chim.*, 1904, [iii], 31, 1055) (compare Inglis and Knight, *loc. cit.*).

In the case of ethyl α -oximinohexanoate, treatment with cold potassium hydroxide furnishes the potassium salt of the ester, the oximino-group thus acting as a negative group; when warmed with two molecular proportions of the alkali, the solution being acidified in the cold, the potassium salt (N·OK) separated, from which the acid was obtained on warming with hydrochloric acid.

Determination of Conductivities.

Owing to alterations in the laboratory being in progress at this time, it was impossible to prepare water with a smaller specific conductivity than 3.3×10^{-6} .

The conductivity measurements were carried out at 25°, and owing in some cases to the rapid decomposition of the acids, together with the high conductivity of the water, measurements were not continued past a dilution of 256. All measurements except those at a dilution of 16 litres were duplicated. Since the conductivity was found to rise with the time, in order to obtain uniformity all measurements were made ten minutes after each successive dilution.

In the case of α -oximino- β -phenylpropionic acid, solution could only be effected by the aid of heat, even at a dilution of N/32. The solution, however, was evidently supersaturated, for after some hours crystals separated from it.

The values for Λ_{∞} were calculated by means of Ostwald's empirical law, making use of the number of atoms in the molecule. The agreement between the values obtained in this way and those obtained from the sodium salt showed sufficient agreement in the case of the lower members to warrant the use of the same method for the higher members of the series (see Inglis and Knight, *loc. cit.*).

Equivalent Conductivities of the Acids. *α -Oximinisovaleric Acid* (m. p. 151.5°). $\Lambda_{\infty} = 378$.

$V =$	16	32	64	128	256
$\Lambda_e =$	48.15	66.5	87.5	110.8	136.8
$K =$	0.116	0.117	0.109	0.094	0.071

Mean value of K from the first three measurements = 0.114. *α -Oximinohexoic Acid* * (m. p. 131—132°. $\Lambda_{\infty} = 377$.

$V =$	32	64	128
$\Lambda_e =$	51.6	69.7	91.9
$K =$	0.0679	0.0656	0.0615

Mean $K = 0.0650$.* The *ethyl* ester, $C_8H_{15}O_3N$, which has not been described, melts at 42°. *α -Oximinoisohexoic Acid* (m. p. 150—151°). $\Lambda_{\infty} = 377$.

$V =$	16	32	64	128	256
$\Lambda_e =$	32.8	47.0	64.1	88.75	119.4
$K =$	0.0515	0.054	0.055	0.057	0.056

Mean $K = 0.056$. *α -Oximino- β -phenylpropionic Acid* (m. p. 163°). $\Lambda_{\infty} = 377$.

$V =$	32	64	128	256
$\Lambda_e =$	49.5	67.7	89.7	118.7
$K =$	0.062	0.061	0.058	0.056

Mean $K = 0.057$. *α -Oximinophenylacetic Acid* (m. p. 127°). $\Lambda_{\infty} = 379$.

Recalculated from Hantzsch and Miolati's results.

$V =$	16	32	64	128	256
$\Lambda_e =$	55.05	75.37	101.48	133.9	172.2
$K =$	0.1536	0.1545	0.1531	0.1508	0.1478

Mean $K = 0.1519$.*Stability of Acids in Aqueous Solution.*

In order to obtain, if possible, some idea of the nature of the decomposition undergone by these acids in solution, an approximately $N/40$ solution of α -oximinisovaleric acid was placed in the thermostat at 25°. The strength of the acid was estimated at intervals by titration with $N/20$ -sodium hydroxide.

The following are the values obtained, 5 c.c. of acid being employed for each titration:

Time in hours ...	0	2.5	3.5	5.5	21.5
Titre in c.c.	2.67	1.7	1.62	1.4	0.8

An attempt to determine the velocity constant for this decomposition was unsuccessful, owing probably to the doubtful nature of the products, of which carbon dioxide is one, but the concentration of which is uncertain. The result therefore only shows the diminution in strength approximately.

Discussion of Results.

Owing to the unstable nature of the higher members of this series of acids, little definite conclusion can be drawn.

The rise of conductivity with the time may mean a change from one isomeride into another, or it may simply mean a gradual decomposition, the conductivity ultimately becoming that of a complex solution.

It seems certain, however, that the oximinic hydroxyl group, rather than acting as an alcoholic group, as was implied by Hantzsch and Miolati, acts negatively, and so would lead to the greater strength of the "syn" acid, not the "anti" modification. There seems to be some anomalies in Hantzsch's conclusions as regards configuration, for (*Ber.*, 1891, 24, 36) he states that the acetyl derivative of the α -oximinophenylacetic acid, melting at 145° , is decomposed by carbonate into the nitrile, carbon dioxide, etc., whilst that melting at 127° gives the original oxime. Since the melting point is a decomposition point, we should expect the "syn" acid to decompose more readily, that is, at the lower temperature. Again (*ibid.*), he states that the "syn" oxime is converted into the "anti" acetyl derivative by the process of acetylation, and since no mention of the preparation of the "syn" oxime is given, it is difficult to accept this as final.

Judging from the above results, and those obtained by Inglis and Knight, it seems, as was stated by these authors in connexion with the lower members, that the relation between configuration and dissociation constants is not so simple as was supposed, and an attempt to utilise the melting point as a means of assisting in the conclusion is just as unsatisfactory in its result.

One might expect to find some relation between the instability of the acids in aqueous solution and the configuration of their molecules; now in the case of α -oximinooisovaleric acid, the strength diminished in twenty-one and a-half hours from 0.031*N* to 0.008*N*, whilst in the case of α -oximinooisohexoic acid, the strength only fell from 0.031*N* to 0.026*N* in twenty-four hours.

Here we have no simple relation in the change of titre, because, applying Bischoff's dynamic theory, the obvious conclusion would be that α -oximinooisohexoic acid would be the less stable of the

two, since the two methyl groups in the 5-position with respect to the hydroxyl of the oximino-group ought to force the hydroxyl and carboxyl groups nearer together and cause instability; but this is inconsistent with the fact that α -oximinoisohexonic acid is one of the easiest to prepare, and it is also fairly stable in aqueous solution, the titre falling off only slightly in twenty-four hours.

On the other hand, α -oximinoisohexonic acid may have the "anti" configuration, and this would be consistent with the fact that α -oximinoisovaleric acid is much stronger than α -oximinoisohexonic acid. α -Oximinophenylacetic acid has a higher dissociation constant than α -oximino- β -phenylpropionic acid. This may be partly due to space relationships and partly due to the negative character of the phenyl group.

According to Bischoff and Hedenström (*Ber.*, 1902, **35**, 4096), it seems that, in general, the phenyl esters are hydrolysed with greater difficulty than the benzyl esters, thus pointing to hindrance due to the closeness of the nucleus; this same closeness would lead to proximity of oximino- and carboxyl groups, and thus to a stronger acid. As regards purely aliphatic acids, however, all that can be said at the present juncture is that there is strong evidence of the oximino-group reacting negatively, but that general conclusions as regards the series are unjustifiable.

My thanks are due to Dr. J. K. H. Inglis, at whose suggestion these experiments were carried out, for his guidance and assistance during the investigation.

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Organic Chemistry.

Revision of the Tables for the Strength of Ethyl Alcohol. N. SCHOORL and (Miss) A. REGENBOGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 831—837, and *Pharm. Weekblad*, 1918, **55**, 390—409).—In view of the preparation of a new edition of the Dutch Pharmacopœia, measurements have been made of the density of mixtures of ethyl alcohol and water at 15°. The results obtained are in agreement with those obtained by Osborne and MacKelvy (compare A., 1912, i, 232), and the authors recommend the table of the Bureau of Standards (Washington) as affording the most accurate values of the densities of alcohol-water mixtures. [See also *J. Soc. Chem. Ind.*, 318A.] H. M. D.

Preparation of Amylene Bromohydrin (Bromoamyl Alcohol). EMIL RATH (D.R.-P., 301905; from *Chem. Zentr.*, 1918, i, 53).—Mixtures of hypobromites and such acids as boric acid yield with amylene (β -methyl- Δ^2 -butylene) in the cold the bromohydrin, which may be useful in the production of pharmaceutical preparations. J. C. W.

New Molybdyl Compound. RICARDO MONTEQUI DÍAZ DE PLAZA (*Anal. Fis. Quim.*, 1910, **14**, 542—548; from *Chem. Abstr.*, 1917, **11**, 2864—2865).—When aqueous solutions of ammonium molybdate and potassium isobutylxanthate are mixed, the liquid after a time assumes a dark violet colour, and when acidified by the gradual addition of acetic acid, a dark-coloured substance, consisting of a mixture of $(C_4H_9OS_2)_4$, Mo_3O_3 and $(C_4H_9OS_2)_2$, is precipitated. When the precipitate is dried and extracted with light petroleum, the latter substance is removed.

The molybdenum compound forms nearly black, monoclinic crystals, m. p. 105°, insoluble in water, slightly soluble with purple colour in cold, and with greenish-blue colour in hot, ethyl alcohol, and readily soluble in acetone, benzene, toluene, carbon disulphide, chloroform, or ethyl ether with intense purple coloration. It is not acted on in the cold by concentrated hydrochloric or sulphuric acid. It is oxidised by nitric acid, and dissolves readily in potassium hydroxide solution, but not in ammonia. H. M. D.

Configuration of Organic Compounds and their Relation to Chemical and Physical Properties. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1918, **40**, 704—723).—A theoretical paper in which the author discusses the relationships between the free and bound energy, and entropy changes with the spacial arrangement of the atoms in stereoisomerides. The influence of olefinoid unsaturation and configuration on the affinity constants of acids is discussed in the cases of aliphatic acids, dibasic unsaturated acids, and the cinnamic acids. J. F. S.

Relative Stabilities of Halogen-substituted Aliphatic Acids in Aqueous Solution. II. The Propionic and Butyric Acid Series. G. S. SIMPSON (*J. Amer. Chem. Soc.*, 1918, **40**, 674—683. Compare this vol., i, 57).—The hydroxylation of halogen derivatives of propionic and butyric acids has been studied by keeping 0.1*N*-solutions of their sodium salts at 70° and titrating the sodium haloid formed at different intervals. The following order of stability is established:—*propionic* acid series: β -bromo-, β -iodo-, α -bromo-, β -chloro-, $\alpha\alpha$ -dibromo-, $\alpha\beta$ -dibromo-, α -chloro-, $\alpha\beta$ -dichloro-, of the order 1, 1.03, 3.31, 7.17, 10.96, 18.68, 37.06, 186.8; *butyric* acid series: α -bromoiso-, β -chloro-, α -bromo-, α -chloro-, of the order 1, 277, 374, 6171.

From these figures, the following points are apparent: (1) chlorine-substituted acids are more stable than analogous bromine or iodine compounds; (2) iodine compounds are sometimes more stable than bromine analogues; (3) α -halogen acids are more stable than their β -isomerides, and position is of greater moment than the nature of the halogen; (4) if the hydrogen atoms in the $-\text{CH}_2\text{Hal.}$ or $-\text{CHHal.}$ groups are replaced by alkyl radicles, the stability of the acids is diminished, and the larger the alkyl group, the greater is the weakening effect; (5) a second halogen atom in the α -position renders the removal of a halogen in the α - or β -position more difficult.

Some brief notes on the preparation of the various acids are given, and the bearing of some of the results on problems connected with the hydrolysis of the salts (compare Senter and others) is discussed. J. C. W.

Synthesis and Oxidation of Tertiary Hydrocarbons.

P. A. LEVENE and L. H. CRETCHER, jun. (*J. Biol. Chem.*, 1918, **33**, 505—512).—The tertiary hydrocarbons are prepared by the reduction of acids obtained by the malonic ester synthesis.

Ethyl dibutylmalonate, $\text{C}(\text{C}_4\text{H}_9)_2(\text{CO}_2\text{Et})_2$, is formed by the action of butyl iodide and sodium ethoxide on ethyl malonate. The introduction of the first butyl radicle must be completed before that of the second is attempted. The attempt to effect both substitutions at the same time by heating the malonic ester with two molecules of the ethoxide and iodide gives unsatisfactory results. Ethyl dibutylmalonate boils at 153—154°/14 mm. (corr.). On saponification, *dibutylmalonic acid*, $\text{C}_{11}\text{H}_{20}\text{O}_4$, is obtained. It crystallises from benzene in long, prismatic needles, m. p. 163° (decomp.). On heating at 180°, carbon dioxide is evolved, and at 255° (corr.), *α -butylthreic acid*, $\text{CH}(\text{C}_4\text{H}_9)_2\cdot\text{CO}_2\text{H}$, distils over; this has b. p. 153°/16 mm. and D_{20}^{25} 0.899. The ester, *ethyl α -butylthreate*, $\text{C}_{15}\text{H}_{24}\text{O}_3$, is prepared by boiling the acid with alcohol and a little sulphuric acid for eight hours, and has b. p. 114—115°/15 mm. (corr.). The reduction of the ester to the corresponding alcohol is accomplished by Levene and Allen's method (A., 1917, i, 3), the yield being 65 to 70% of that theoretically possible. *β -Butyltheryl alcohol*, $\text{C}_{10}\text{H}_{20}\text{O}$, has b. p. 218—219°

orr.) and D 0.836. On boiling the alcohol with three molecules hydriodic acid for five hours, an 80% yield of β -butylhexyl iodide, $C_{10}H_{21}I$, is obtained, b. p. 124–125°/13 mm., D 1.267, and duction of the iodide with zinc and glacial acetic acid yields butylhexane, $C_{10}H_{22}$, b. p. 165° (corr.), D 0.738.

When β -butylhexyl iodide is slowly added to an excess of the monosodium derivative of ethyl malonate in alcohol and the mixture boiled, ethyl β -butylhexylmalonate, $C_{17}H_{35}O_4$, b. p. 180°/1 mm., is produced, which on saponification yields β -butylhexylmalonic acid, $C_{13}H_{24}O_4$, rhombic needles from light petroleum, m. p. 88° (corr.). The following compounds are prepared by the methods already indicated in the case of the β -butylhexane derivatives: γ -butyloctioic acid, $C_{12}H_{24}O_2$, b. p. 173–174°/12 mm. (corr.), D 0.901; ethyl γ -butyloctoate, $C_{14}H_{28}O_2$, b. p. 139°/10 mm. (corr.); δ -butyloctyl alcohol, $C_{12}H_{26}O$, b. p. 139°/15 mm., D 0.841; and δ -butyloctyl iodide, $C_{12}H_{25}I$, b. p. 143°/8 mm., D 1.194.

β -Butylhexane is readily oxidised at 80–90° by an alkaline solution of permanganate, but the only oxidation products which can be detected are formic acid and carbon dioxide. At 25°, a small amount of butyric acid is formed, which is recognised by its silver salt.

H. W. B.

Preparation of Acetaldehyde. H. DREYFUS (Brit. Pat. 15064).—Acetylene which has been freed from such impurities as hydrogen sulphide, hydrogen phosphide, and ammonia, is passed, under a pressure of about 1.5 atm., into a solution containing 3–15% of sulphuric acid and from 1 to 10%, preferably 3–6%, of mercury. The liquid is kept at 25–40°, and the gas is passed slowly, with vigorous agitation, until the precipitated mercury compound becomes grey or greyish-black, and then as rapidly as the liquid will absorb it. At intervals, the temperature is raised, not above 50–60° to distil off the acetaldehyde. A yield of acetaldehyde equivalent to 90–95% of the quantity of acetylene, five to ten times that of the mercury compound used, is obtained. See, further, *J. Soc. Chem. Ind.*, 1918, 222A.] A. S.

The Crotonisation of Acetaldehyde. Formation of Butanol and Hexanol from Ethyl Alcohol. PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1918, 166, 632–636).—Acetaldehyde when passed over the oxides of thorium, titanium, or uranium at 360° undergoes crotonisation and gives crotonaldehyde, hexadienaldehyde, and a certain amount of higher homologues. If ethyl alcohol is used as the starting material, it is passed first over reduced copper at 300°, and the resulting vapours are then passed over uranium oxide at 360°, or the vapours of the alcohol may be passed slowly over uranium oxide at 360°, when they undergo dehydrogenation and dehydration in the one process. The best yield of crotonaldehyde is obtained by vaporising acetaldehyde and passing these vapours over the catalyst. If the products of the crotonisation are roughly fractionally distilled and the fractions boiling at about 90–130° and 130–220° passed

with hydrogen over reduced nickel at 170—180°, normal butyl alcohol and normal hexanol are obtained. W. G.

Acetone and Lime. M. E. FREUDENHEIM (*J. Physical Chem.*, 1918, **22**, 184—193).—When acetone vapour is passed over slaked lime in a tube heated at temperatures varying from 350° to 630°, calcium carbonate and carbon are left in the tube, the amount of carbon being small at low temperatures, but rapidly increasing with a rise in temperature. The gas evolved consists of methane, hydrogen, carbon monoxide, ethylene, and carbon dioxide. The amount of gas decreases during the run, and the percentage of hydrogen also shows a tendency to decrease, whilst the percentage of methane increases; the percentages of carbon monoxide and olefines remain practically constant at 16% and 4% respectively. At 350°, the gaseous products are nearly 80% hydrogen and 20% methane; at 650° methane is the chief gaseous product.

It is thought that acetone may be an intermediate product of the action of lime on calcium acetate, and that its dissociation may account for the presence of carbon monoxide, thus: $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 = \text{CH}_4 + \text{CO} + \text{C} + \text{H}_2$, whilst the ethylene may owe its formation to the production of methane and kelen, the latter breaking down into carbon monoxide and ethylene, thus: $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 = \text{CH}_4 + \text{CH}_2\cdot\text{CO}$, $2\text{CH}_2\cdot\text{CO} = 2\text{CO} + \text{C}_2\text{H}_4$. The production of hydrogen and methane only at 350° cannot be accounted for satisfactorily, though it is known that hydrogen is also set free when sodium acetate is heated with soda lime.

When acetone is passed over heated nickel, carbon is precipitated and some of the excess of acetone is reduced to isopropyl alcohol, and it is stated that the decreasing percentage of hydrogen evolved at higher temperatures is probably due to its action on the acetone, with formation of isopropyl alcohol. [See also *J. Soc. Chem. Ind.*, 1918, 282A.] B. N.

Synthesis of Two Isomeric Series of Alkylthioglucosides.

WILHELM SCHNEIDER, JOHANNA SEPP, and OTTILIE STIEHLER (*Ber.*, 1918, **51**, 220—234. Compare A., 1916, i, 792).—The reaction by which glucose mercaptals may be converted into alkylthioglucosides, namely, by treatment with one molecular proportion of mercuric chloride, has been extended from the ethyl to the methyl, *n*-propyl, and benzyl compounds. The products obtained in this way happen to be all α -glucosides, but the isomeric β -glucosides can also be formed, the mode of preparation depending on the interaction of the potassium salts of mercaptans with acetobromoglucose. Compared with the α - and β -methylglucosides, the two series of thioglucosides show a remarkable difference; the β -isomerides are much more stable towards dilute mineral acids than the α -compounds in this case. The thioglucosides are also non-acidic, whereas the mercaptals dissolve in alkali hydroxides.

The new mercaptals were again prepared by Fischer's method, namely, condensation of glucose with the thiol under the influence

of concentrated hydrochloric acid. *Glucose methyl mercaptal*, $C_6H_{12}O_5(SMe)_2$, has m. p. 161° , $[\alpha]_D^{20}$ in *N*-sodium hydroxide, -20.76° , and forms a *penta-acetate*, m. p. 83° , $[\alpha]_D^{20}$ in *s*-tetrachloroethane, $+38.71^\circ$; α -*methylthioglucoside*, $C_6H_{11}O_5SMe$, crystallises in slender needles, m. p. 137° , $[\alpha]_D^{20}$ in water, $+124.5^\circ$, and its *tetra-acetate* has m. p. 89° , $[\alpha]_D^{20}$ in *s*-tetrachloroethane, $+150.0^\circ$. *Penta-acetylglucose ethyl mercaptal*, m. p. $42-45^\circ$, $[\alpha]_D^{20} +17.71^\circ$, is very stable towards mercuric chloride, and cannot be converted by its agency into the tetra-acetyl derivative of true, aldehydic glucose. *Glucose n-propyl mercaptal* forms slender leaflets, m. p. 146° , and α -*n-propylthioglucoside* has m. p. $118-122^\circ$, $[\alpha]_D^{20}$ in water, $+116.5^\circ$. α -*Benzylthioglucoside* has m. p. $112-114^\circ$ (viscous), 118° (mobile), $[\alpha]_D^{20} +175.7^\circ$, and forms a *tetra-acetate*, prismatic needles, m. p. 77° , $[\alpha]_D^{20} +186.3^\circ$; *penta-acetylglucose benzyl mercaptal* has m. p. 64° , $[\alpha]_D^{20} +31.75^\circ$.

The hydrolysis of α -ethylthioglucoside has been examined. It is unaffected by maltase, emulsin, or myrosin; with 1% hydrochloric acid at 25° , equilibrium is reached in thirty-four hours, when 94–95% has been hydrolysed, but with 2.5% hydrochloric acid, the same result is obtained in eight to nine hours.

Acetobromoglucose and potassium methyl sulphide react in methyl-alcoholic solution to form *tetra-acetyl- β -methylthioglucoside*, slender needles, m. p. 93° , $[\alpha]_D^{20}$ in *s*-tetrachloroethane, -14.67° , which is hydrolysed by barium hydroxide solution in the cold to β -*methylthioglucoside*, a syrup with $[\alpha]_D^{16} -18.14^\circ$. Partial hydrolysis takes place in the first stage, so the crude product is heated with acetic anhydride and sodium acetate before purification. *Tetra-acetyl- β -ethylthioglucoside* crystallises in needles, m. p. $78-79^\circ$, $[\alpha]_D^{20} -22.27^\circ$, and forms a compound, m. p. $83-84^\circ$, with ordinary tetra-acetyl- β -ethylglucoside; β -*ethylthioglucoside* forms stout, rectangular prisms, $1H_2O$, m. p. $46-47^\circ$, the anhydrous substance having m. p. $99-100^\circ$, $[\alpha]_D^{16} -55.14^\circ$. *Tetra-acetyl- β -benzylthioglucoside* has m. p. 98° , $[\alpha]_D^{24} -93.1^\circ$, and β -*benzylthioglucoside* is a syrup.

β -Ethylthioglucoside is unaffected by emulsin, myrosin, or maltase, and is not perceptibly altered by hydrochloric acid unless the concentration is at least 5% and the temperature $70-80^\circ$.

J. C. W.

Structure of Crystalline β -Methylfructoside. ETTIE STEWART STEELE (T., 1918, 113, 257–263).—Recent investigations (Irvine and Robertson, A., 1917, i, 79) have shown that it is very probable that the syrup obtained by condensing fructose with methyl alcohol contains the α - and β -modifications of both butylene-oxidic and ethylene-oxidic methylfructosides. The mixture may be methylated by means of silver oxide and methyl iodide, and the product converted by hydrolysis into a mixture of tetramethylfructoses, consisting of a crystalline and a syrupy variety (Purdie and Paul, T., 1907, 91, 289). The same crystalline tetramethylfructose has now been obtained by similar treatment of Hudson's

crystalline β -methylfructoside (A., 1916, i, 547), which is stable towards permanganate, that is, conforms to the butylene oxide type. The crystalline tetramethylfructose must therefore be butylene-oxidic, or, in other words, the original mixture of β -methylfructosides contains Hudson's γ -oxidic isomeride.

The action of acetic anhydride on fructose, in the presence of zinc chloride, yields about equal quantities of crystalline and syrupy products. The solid portion is stable towards permanganate, and is the tetra-acetate from which Hudson prepared his β -methylfructoside. It may be acetylated completely, and is derived, therefore, from butylene-oxidic fructose. The syrup is apparently a triacetate, which resists further acetylation, may be converted into a mono-methyl ether (not a methylfructoside triacetate), and very readily reduces permanganate. It is therefore derived from ethylene-oxidic fructose.

J. C. W.

Preparation of a Salt of Fructosediphosphoric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 302094; from *Chem. Zentr.*, 1918, i, 249).—The calcium salt of fructosediphosphoric acid (from metaphosphoric esters and fructose) is only sparingly soluble, but is, nevertheless, easily absorbed in the organism, and is claimed to be good in such cases as rickets.

J. C. W.

The Digestibility of Bread. III. Erythrodestrin in Starch Hydrolysis. J. C. BLAKE (*J. Amer. Chem. Soc.*, 1918, 40, 623–636. Compare A., 1916, i, 578; 1917, i, 361).—In the previous communication, it was shown that the digestion of erythrodestrin is a unimolecular reaction. It might therefore be used in order to determine amylolytic activity, and, consequently, efforts have been made to obtain pure erythrodestrin for such purposes. In this connexion, the present paper describes some new studies on the degradation of starch by (a) heating starch moistened with 0.1*N*-hydrochloric acid at 85°, and (b) boiling starch with about 0.032*N*-hydrochloric acid, and also new methods for estimating the products by measuring the colorations produced by iodine water. It is expected that it will soon be possible to prepare pure erythrodestrin.

It appears that the cleavage of boiled starch takes place in at least three stages, protein and amylodestrin preceding erythramylum (rose-amylose) and erythrodestrin in order of formation. These stages probably correspond with the stages of salivary digestion and the degradation by roasting.

A number of supplementary notes are recorded. (1) "Artificial starch," the substance which crystallises at about 50° on cooling a partly hydrolysed solution of starch, is a solid solution of amylodestrin and erythrodestrin in higher polysaccharides. (2) Lintner's "soluble starch" is almost pure amylodestrin, crystallising with difficulty only at temperatures below 50°, and forming an iodide, the transition temperature of which, in 1% solutions, is 69.5°. (3) Amylodestrin appears to be an individual substance, fairly

soluble in cold water, but not in 40% alcohol; it gives a blue iodide which has the maximum transition point, 74° ; it probably yields erythrodestrin on hydrolysis. (4) Erythrodestrin is insoluble in 49–67% alcohol; the transition point of its iodide is 64° ; it yields achroodestrin on hydrolysis, but in the "roasting" process it appears to be the final polysaccharide. (5) Erythramylum is formed simultaneously with erythrodestrin, and probably changes into amylodestrin on hydrolysis; it is precipitated by 35% alcohol.

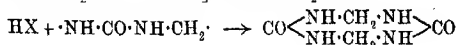
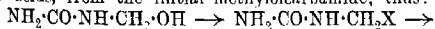
J. C. W.

Preparation of Taurine in Large Quantities. CARL L. A. SCHMIDT and THOMAS WATSON (*J. Biol. Chem.*, 1918, **33**, 499–500).—Taurine is readily prepared from the abalone, *Haliotis*, which can be obtained in quantity on the Pacific coast. The shell and intestinal tract are removed, and the muscle is then finely minced and the juice pressed out. Protein is removed from the juice by precipitation with acetic acid, and the filtrate hydrolysed with hydrochloric acid. After concentration, the taurine is precipitated by alcohol, and finally recrystallised from water. Eight dozen abalones (74 kilograms of muscle) yield 362 grams of taurine.

H. W. B.

Interaction of Formaldehyde and Carbamide. AUGUSTUS EDWARD DIXON (T., 1918, **113**, 238–248).—A number of experiments on the condensation of carbamide with formaldehyde (37.5% solution) are described. Equimolecular proportions, just neutralised with dilute sodium hydroxide, yield on evaporation in a desiccator methylolcarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, which gives no reaction for formaldehyde unless acidified. With a double proportion of formaldehyde, under the same conditions, the product is dimethylolcarbamide, $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{OH})_2$, which changes at about 123° or when treated with dilute hydrochloric acid into the compound, $\text{CO}\begin{smallmatrix} \text{NH} & \text{CH}_2\cdot\text{NH} \\ \diagdown & \diagup \\ & \text{N}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}_2\cdot\text{NH} \end{smallmatrix}\text{CO}$, thus, $2\text{C}_3\text{H}_8\text{O}_3\text{N}_2 \rightarrow \text{C}_3\text{H}_{10}\text{O}_3\text{N}_4 + \text{CH}_2\text{O} + 2\text{H}_2\text{O}$. The two methylol derivatives have already been described by Einhorn and Hamburger (A., 1908, i, 141), and the third product is Goldschmidt's compound (A., 1897, i, 22; 1898, i, 178).

When condensation between formaldehyde and carbamide is catalysed by small quantities of acids, granular precipitates usually appear very quickly. They vary in composition, but display as a common feature black crosses in plane polarised light. With 0.75 mol. of formaldehyde, the product is dimeric methylene-carbamide, presumably formed, in the presence of small quantities of acids, from the initial methylolcarbamide, thus:

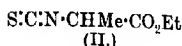
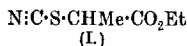


With 1.5 to more than 2 mols., the sole product is Goldschmidt's compound, probably formed by the action of formaldehyde on

"nascent" monomeric methylenecarbamide. With 4 mols., the precipitate is scanty and consists of a substance probably of the formula $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH})_2$, whilst with 11 mols. condensation ceases.

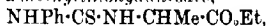
J. C. W.

Thiocyanates and Thiocarbimides. XII. The Polyketide Thiocarbimide, Ethyl α -Thiocarbiminopropionate. TREAT B. JOHNSON and ARTHUR A. TICKNOR (*J. Amer. Chem. Soc.*, 1900, **40**, 636—646. Compare A., 1916, i, 635, 717).—Inactive ethyl α -thiocyanopropionate (I) was prepared by Wheeler and Barnes from the α -bromopropionate and potassium thiocyanate (A., 1900, i, 566). The inactive and dextrorotatory forms of the isomeric ethyl α -thiocarbiminopropionate (II) have now been obtained by the interaction of thiocarbonyl chloride and the ethyl α -aminopropionates.



Racemic alanine hydrochloride is most conveniently prepared by conducting the crude acetaldehyde from the oxidation of alcohol directly into a solution of commercial sodium cyanide, ammonium chloride, and ammonia, and after twenty-four hours acidifying and evaporating to dryness. The free ester (3 mols.) reacts vigorously with thiocarbonyl chloride (1 mol.) in dry ether, and the hydrochloride reacts with rather more than one molecular proportion of thiocarbonyl chloride in boiling toluene, giving the hydrochloride of ethyl dl- α -thiocarbiminopropionate, m. p. 87°. The free ester, obtained on distillation of the salt, is a pale yellow oil, b. p. 93.5—94.5°/13 mm., D 1.0994 (average), n_D^{20} 1.4915. Similarly, active alanine ester hydrochloride gives rise to ethyl d- α -thiocarbiminopropionate, b. p. 100—101°/11—12 mm., n_D^{20} 1.4935, $[\alpha]_D^{20} + 29.77^\circ$, but the free amino-acid does not react in this way.

As a thiocarbimide, the inactive ester reacts with aniline to form ethyl phenyl- α -methylthiohydantate,



which crystallises in rosettes, m. p. 83—84°. Inactive ethyl alanine and phenylthiocarbimide apparently produce the same compound, but the reaction is so vigorous that this loses alcohol, and so the actual product is 2-thio-1-phenyl-4-methylhydantoin, $\text{CS}\begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ \text{NH}\cdot\text{CHMe} \end{smallmatrix}$, m. p. 183.5—184.5° (compare Aschan, A., 1883, 1107).

Furthermore, the ester reacts with hot alcohol to form the thionurethane, $\text{OEt}\cdot\text{CS}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, in slender prisms, m. p. 55.5—56°, b. p. 157—159°/18 mm.

J. C. W.

New Preparation of Nitriles by Catalysis of Primary Amines. ALPH. MAILHE and F. DE GÉDON (*J. Pharm. Chim.*, 1917, [vii], 16, 225—229).—A claim for priority over Sabatier and

Gaudion (compare A., 1917, ii, 460) for the use of reduced copper or reduced nickel as catalysts for the conversion of primary amines into the corresponding nitriles. The present authors had deposited the details of their process in a sealed communication in March, 1917. W. G.

Preparation of Halogenated Arsinic Acids. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P., 296915; from *Chem. Zentr.*, 1917, i, 715).—Hydrocarbons of the acetylene series are treated with arsenic trihaloids, or mixtures which yield these compounds, and the products are converted into arsenoxides and then into arsinic acids by oxidation. Thus, heptinene gives "heptinene-chloroarsenoxide," a dark syrup, and "heptinenechloroarsinic acid" [β , β -chloro- Δ^2 -heptenylarsinic acid, $C_7H_{11} \cdot CCl:CH \cdot AsO(OH)_2$], white needles, m. p. 115° , the sodium salt of which is freely soluble in water. Octinene yields "octinenebromoarsenoxide" and "octinenebromoarsinic acid" [β , β -bromo- Δ^2 -octenylarsinic acid], m. p. $129-130^\circ$. J. C. W.

Werner's Theory of Valency and Benzene. A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, 15, 400-405).—The author is of opinion that Werner's theory of valency is not adapted to account for the structure and properties of benzene and its derivatives.

A. J. W.

Sulphite Turpentine. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1918, 10, 258-260).—The so-called sulphite turpentine, obtained as a by-product in the manufacture of wood pulp by the sulphite process, consists in the main of cymene, and may be utilised in the production of toluene and carvacrol. Cymene-2-sulphonic acid forms a characteristic barium salt, $(C_{10}H_{18}SO_3)_2Ba \cdot 3H_2O$, which is sparingly soluble in water and crystallises in lustrous plates. On heating the anhydrous barium salt of the 2-sulphonic acid with an equal weight of phosphorus pentachloride, and forming the amide by heating with ammonia, a yield of 70.7 per cent. of the theoretical amount of cymenesulphonamide, m. p. 114° , was obtained. By oxidation with potassium permanganate, the cymene was converted into *p*-hydroxyisopropylbenzoic acid, m. p. 155° . Cymene also reacts readily with chlorosulphonic acid, and the resulting product may be converted into the sulphonamide by heating it with strong ammonia solution on the boiling water-bath. This reaction affords a convenient method of identifying pure cymene. When the sodium salt of cymene-2-sulphonic acid is fused with alkali at about 300° , carvacrol is produced in small quantity, and may be purified by converting it into carvacrol nitrite, m. p. $150-152^\circ$, which is insoluble in light petroleum. [See also *J. Soc. Chem. Ind.*, 296a.] C. A. M.

Steric Hindrance. IV. J. VON BRAUN, Z. ARKUSZEWSKI, and Z. KÖHLER (*Ber.*, 1918, 51, 282-296).—Comparing dimethyl-*q*-

group, are white powders, practically tasteless and odourless, generally sparingly soluble in water, and of value as anthelmintic remedies. *p*-Benzylphenyl carbamate, crystals (from alcohol), m. p. 144°, is specifically claimed. *p*-Butylphenyl carbonate melts at 108°, *p*-isoamylphenyl carbamate at 73–74°, *p*-butylphenyl carbamate at 123–124°, *p*-isopropylphenyl carbamate at 93–95°, *p*-butylphenyl *N*-dimethylcarbamate at 92°, and *o*-allylphenyl carbamate at 122–123°. A. S.

Synthesis of 3:4-Dihydroxyphenanthrene (Morphol) and of 3:4-Phenanthraquinone. GEORGE BARGER (T., 1918, 113, 218–221).—3-Phenanthrol-4-aldehyde (A., 1916, i, 487) dissolved in pyridine reacts vigorously with hydrogen peroxide and potassium hydroxide to form morphol in excellent yield. The method is a modification of Dakin's process for converting *o*- and *p*-hydroxy-aldehydes into dihydric phenols (P., 1909, 25, 194). The oxidation of morphol to 3:4-phenanthraquinone may be achieved by means of dry silver oxide in ether.

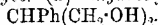
For experimental details, see the original.

J. C. W.

Preparation of Condensation Products from Aromatic Hydroxysulphonic Acids. BADISCHE ANILIN & SODA-FABRIK (D.R.-P., 301451; addition to 300567; from *Chem. Zentr.*, 1917, i, 787).—Phenolic mono- or di-alcohols are condensed with aromatic hydroxysulphonic acids, or with aromatic hydroxy-compounds followed by sulphonation of the products. For example, β -naphthol-6-sulphonic acid is condensed with *p*-homosaligenin, *p*-cresol with *p*-cresoldialcohol (the product has m. p. 215°), and 2-chloro- α -naphthol with *p*-homosaligenin and dihydroxyditolylmethane (m. p. 126°; from formaldehyde and *p*-cresol).

J. C. W.

Condensation of Unsaturated Systems. H. J. PRINS (*Chem. Weekblad*, 1917, 14, 932–939).—In addition to the matter referred to in A., 1917, i, 685, this paper contains a description of *B*-phenyltrimethylene glycol (α -*dihydronymene*).



This is formed to the extent of 70%, together with some polymeric styrene, by the action of formaldehyde on styrene, $\text{CHPh}:\text{CH}_2 + \text{H}\cdot\text{COH} + \text{H}_2\text{O} = \text{CHPh}(\text{CH}_2\text{OH})_2$. It is a colourless oil, b. p. 145°/12 mm. When heated with acetic anhydride, it is converted quantitatively into the *acetate*, $\text{CHPh}(\text{CH}_2\text{OAc})_2$, b. p. 178°/12 mm.

Preparation of β -Naphthyl Benzoate. ANTHONY-HAMMOND CHEMICAL WORKS (U.S. Pat. 1254970).—One hundred and ten grams of β -naphthol are heated, and about 170 grams of benzoyl chloride are stirred in, drop by drop, any of the benzoyl chloride which is volatilised being condensed and returned, whilst the hydrogen chloride formed is allowed to escape. A. S.

Preparation of 6-Amino-3-sulphobenzoic Acid. FARBER. FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P., 296941; from *Chem. Zentr.*, 1917, i, 717).—Anthranilic acid is directly sulphonated by means of chlorosulphonic acid in an indifferent solvent, such as nitrobenzene, dichlorobenzene, or petroleum. J. C. W.

***m*-Nitrocinnamic Acid, Brominated in the Side Chain.** S. REICH [with AGAMIRIAN, S. KOEHLER, J. GAJKOWSKI, and (MLE.) E. LUBECK] (*Arch. Sci. phys. nat.*, 1918, 45, 191—216, 259—276).—A more detailed account of work already published (compare A., 1914, i, 41). The following additional compounds are described.

The acid described as β -bromo-*m*-nitrocinnamic acid, m. p. 177—179°, has m. p. 184°, and is really the *allo*-acid, giving a *methyl* ester, m. p. 100—101°, and being converted by the action of light into a stable *stereoisomeride*, m. p. 132°, giving a *methyl* ester, m. p. 75—76°.

α -Bromo-*m*-nitroallocinnamic acid when reduced in aqueous barium hydroxide solution with ferrous sulphate yielded a compound, brown needles, m. p. 206°. The *isomeride*, m. p. 217°, when similarly reduced, yielded *m*-aminophenylpropionic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{H}$, m. p. 183°. On bromination, α -bromo-*m*-nitroallocinnamic acid yielded $\alpha\alpha\beta$ -tribromo- β -*m*-nitrophenylpropionic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CBr}_2\cdot\text{CO}_2\text{H}$, m. p. 157°, giving a *methyl* ester, m. p. 107—110°. On warming with aqueous sodium carbonate, this acid yielded $\beta\beta$ -dibromo-*m*-nitrostyrene, m. p. 58°, which on bromination gave $\alpha\beta\beta\beta$ -tetrabromo-*m*-nitrophenylethane, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CBr}_3$, m. p. 87°. β -Bromo-*m*-nitrocinnamic acid on bromination yielded $\alpha\beta\beta$ -tribromo- β -*m*-nitrophenylpropionic acid, m. p. 165°, giving a *methyl* ester, m. p. 94—95°.

Attempts to esterify *m*-nitrophenylpropionic acid by the action of hydrogen chloride in the presence of methyl alcohol yielded *methyl* β -chloro-*m*-nitrocinnamate, m. p. 113—114°.

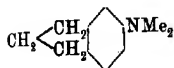
The cuprous derivative of *m*-nitrophenylacetylene (*loc. cit.*), like the derivatives of phenylacetylene and *o*-nitrophenylacetylene, is oxidised by potassium ferricyanide, giving dinitrophenyldiacetylene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{C}:\text{C}:\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, m. p. 149—150°, which gives a tetrabromo-derivative, m. p. 160—161°. *m*-Nitrophenylacetylene when brominated in chloroform solution gave a mixture of *cis*- $\alpha\beta$ -dibromo-*m*-nitrostyrene, m. p. 50—51°, and its *trans*-isomeride, m. p. 79°. These two isomerides on further bromination yielded $\alpha\alpha\beta\beta$ -tetrabromo-*m*-nitrophenylethane,

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CBr}_2\cdot\text{CHBr}_2$, m. p. 96—97°. This compound or its isomeride (see above) when treated in alcoholic solution with the theoretical quantity of potassium hydroxide yielded $\alpha\beta\beta$ -tribromo-*m*-nitrostyrene, m. p. 90°.

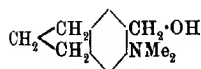
cis- $\alpha\beta$ -Dibromo-*m*-nitrocinnamic acid, m. p. 135—136°, gave a *methyl* ester, m. p. 88°, and its *trans*-isomeride gave a *methyl* ester, m. p. 118—119°.

Similarly, *dimethyl-2-p-xylylidine* (VI), b. p. 204° (*picrate*, m. p. 158°; *platinichloride*, m. p. 196°) reacts almost as sluggishly as *dimethyl-o-toluidine* with methyl iodide, forming the *methiodide*, m. p. 202°, but yields *4-dimethylamino-2:5-dimethylbenzyl alcohol* when condensed with formaldehyde, this being a pale yellow, very viscous oil, b. p. 168—170°/20 mm., which gives a *picrate*, m. p. 114°, a *methiodide*, m. p. 180°, and a *platinichloride*, m. p. 188°.

The conclusion is therefore drawn that the nitrogen atom and para-carbon atom are so inert in *dimethyl-o-toluidine* because the *o*-methyl group and the nitrogen atom are linked by residual affinity. This link is weakened if a meta-substituent is introduced, as the ortho- and meta-groups will then be similarly united, and the nitrogen atom will be more free to react. There is not so much likelihood of a union between a para-substituent and the nitrogen atom, and therefore a meta-group should not have much influence on the activities of a para-substituted tertiary amine. This point has been tested in the case of the base (annexed formula), which actually resembles *dimethyl-p-toluidine* in reactions.



The base is synthesised as follows: technical indene is hydrogenated in the presence of palladous chloride, the hydroindene is nitrated at -5°, the mixture of much *m*- with little *o*-nitrohydroindene is reduced with iron powder and acetic acid, and the mixture of primary amines is warmed with methyl iodide and sodium carbonate. A small quantity of *o*-dimethylaminohydroindene, b. p. 130—131°/20 mm. (*picrate*, m. p. 147°; *platinichloride*, m. p. 185—186°; *methiodide*, m. p. 202°), is formed, but the main product is the *quaternary iodide*, leaflets, m. p. 190°, of the desired *m*-dimethylaminohydroindene (above). This is obtained by distilling the methiodide, as an oil, b. p. 136—138°/18 mm., which forms a *picrate*, m. p. 160—161°, a *platinichloride*, m. p. 170—175°, a red *nitro*-compound, m. p. 85—86°, and a *thiocarbamide* derivative, m. p. 118°, and reacts with formaldehyde and concentrated hydrochloric acid to yield



5-dimethylamino-6-hydroxymethylhydroindene (annexed formula). The latter is a very viscous, pale yellow liquid, b. p. 200°/31 mm., which gives a *picrate*, m. p. 144°, a *platinichloride*, m. p. 178° (decomp.), and a *methiodide*, m. p. 177°.

J. C. W.

Preparation of Tertiary Amines. OSKAR MATTER (D.-R.P., 301450 and 301832; from *Chem. Zentr.*, 1918, i, 53; 149).—Chlorine derivatives of the hydrocarbons are heated with sodamide, the mixture being stirred, and, if necessary, agents like copper gauze or copper powder being employed as catalysts. Thus, chlorobenzene yields triphenylamine, benzyl chloride at 110—120° gives

p**

tribenzylamine, and *iso*amyl chloride at 210—220° forms tri-*iso*-amylamine.

Mixtures of the chlorine compound and a primary amine may also be heated with sodamide, when, if the amine contains a different radicle, a mixed *tert*-amine results. Thus, benzyl chloride, benzylamine, and sodamide, at 100—110°, yield tribenzylamine, benzyl chloride and aniline produce dibenzylaniline, and benzyl chloride and *p*-toluidine give dibenzyl-*p*-toluidine.

J. C. W.

Preparation of a Sparingly Soluble Complex Compound from Dimethylaniline, Benzyl Chloride, and Zinc Chloride.

CHEMICAL WORKS, ROHNER & Co. (Brit. Pat. 104676).—A mixture of one molecular proportion of benzyl chloride and of dimethylaniline respectively is stirred with an aqueous solution of rather more than half a molecular proportion of zinc chloride until the separation of crystals of phenylbenzyl-dimethylammonium zinc-chloride is complete.

A. S.

Separation of Cresols. G. A. DARZENS (Brit. Pat. 107961).—*p*-Cresol and *m*-cresol are separated from mixtures by converting them into additive products with oxalic acid and with anhydrous sodium acetate respectively in the presence of a suitable solvent and with exclusion of moisture. The additive product is separated by filtration and subsequently decomposed by water. If *o*-cresol is also present, it is separated by a preliminary fractional distillation in a vacuum. [See, further, *J. Soc. Chem. Ind.*, 1912, 235A.]

A. S.

Preparation of Carbamic Esters and their N-Alkyl Derivatives, and Carbonic Esters. FARBENFABRIKEN VORM.

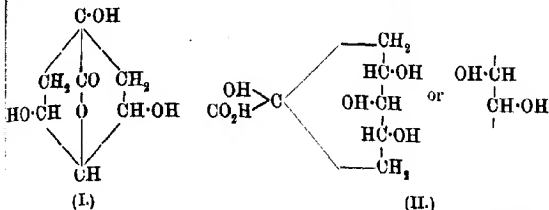
FRIEDR. BAYER & Co. (D.R.-P., 296889; from *Chem. Zentr.*, 1911, i, 714).—Homologues of phenol, except the cresols, are converted into carbonates or carbamates in the usual way. The products are odourless and tasteless, and have anthelmintic properties. Thus, *p*-*tert*-butylphenol reacts with carbonyl chloride to form *p*-*tert*-butylphenyl carbonate, $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_3)_2$, m. p. 108°, in the presence of pyridine, and *p*-*tert*-butylphenyl *N*-dimethylcarbamate, $\text{NMe}_2\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_3$, m. p. 92°, in the presence of dimethylamine, whilst the corresponding carbamate crystallises in platelets or needles, m. p. 123—124°. *p*-*iso*Amylphenyl carbamate has m. p. 73—74°, *p*-benzylphenyl carbamate, m. p. 144°, *p*-*iso*propylphenyl carbamate, m. p. 93—95°, and *o*-allylphenyl carbamate, m. p. 122—123°.

J. C. W.

[*p*-Benzylphenyl Carbamate.] SYNTHETIC PATENTS CO. (U.S. Pat. 1252452).—The carbonyl derivatives of phenols, of the general formula $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{R}'$, in which R is a substituent with more than one carbon atom and R' is $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{R}$ or NXX' , X and X' being respectively either a hydrogen atom or an alkyl

Constitution and Spatial Formula of Quinic Acid.

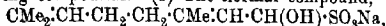
HERMANN EMDE (*Apoth. Zeit.*, 1917, **32**, 601—602; from *Chem. Zentr.*, 1918, i, 208).—From the known physical properties of quinic acid, the author draws the conclusion that the substance is 2:3:4:5-tetrahydroxyhexahydrobenzoic acid. Quinide is the β -lactone (I), and *l*-quinic acid is represented by the formula II.



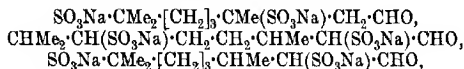
J. C. W.

Hydrosulphonic Derivatives of Citral. GIOVANNI ROMEO

(*Gazzetta*, 1918, **48**, i, 45—52. Compare Tiemann and Lemme, A., 1899, i, 248).—With sodium hydrogen sulphite, citral forms the following compounds. (1) The normal compound,



obtained in presence of a sufficient quantity of free acid, for instance, acetic acid, is crystalline and yields citral when treated with sodium hydroxide solution. (2) The stable dihydrosulphonic derivative, $\text{C}_9\text{H}_{17}(\text{SO}_3\text{Na})_2\cdot\text{CHO}$, formed quantitatively when the normal compound is left for some hours in contact with sodium hydrogen sulphite solution maintained acid in reaction, is highly deliquescent, contains the aldehyde group unchanged, and is not decomposed by alkali hydroxide, even in the hot. Its constitution is represented by one of the four formulæ:



and $\text{CHMe}_2\cdot\text{CH}(\text{SO}_3\text{Na})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_3\text{Na})_2\cdot\text{CHO}$. (3) The labile dihydrosulphonic derivative, $\text{C}_9\text{H}_{17}(\text{SO}_3\text{Na})_2\cdot\text{CHO}$, formed quantitatively when aqueous sodium hydrogen sulphite is shaken with citral and the alkali neutralised as it is formed, is crystalline and of neutral reaction, and is decomposed by alkali into citral and sodium hydrogen sulphite; by mineral or organic acids, it is slowly transformed into the stable modification. Its structure corresponds with one of the four formulæ given for the stable form. (4) Sodium citraldihydrosulphonate, $\text{C}_9\text{H}_{16}(\text{SO}_3\text{Na})\cdot\text{CHO}$, formed from citral and the labile dihydrosulphonate, is a solid, and immediately yields citral when treated in aqueous solution with potassium hydroxide. (5) Labile sodium citraltrihydrosulphonate, $\text{C}_{10}\text{H}_{18}\text{O}(\text{SO}_3\text{Na})_3$, obtained from citral, sodium sulphite, and sodium hydrogen sulphite, is odourless, non-deliquescent, and of

neutral reaction, and is accompanied by a small proportion of (6), an isomeride stable towards potassium hydroxide.

T. H. P.

Preparation of β -Aminoanthraquinone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1255719).— β -Anthraquinonemonsulphonic acid is heated with ammonia and an aromatic nitro-compound, yielding β -aminoanthraquinone and the amino-compound corresponding with the nitro-compound used.

A. S.

Crystallographic and Optical Characters of Amyrolin. HERMANN ROSE (*Jahrb. Min.*, 1918, 1—18).—Amyrolin, $C_{14}H_{12}O_2$ (von Soden and Rojahn, A., 1901, i, 159), has $D^{18}_D = 1.351$ and m. p. $119-124^\circ$. The crystals are monoclinic, $a:b:c = 0.7583:1:1.1106$; $\beta = 76^\circ 55'$. The optical constants are given for wave-lengths 690.7 to 404.7μ . For sodium light, $\alpha = 1.46447$, $\beta = 1.74738$, $\gamma = 1.94579$, $\gamma - \alpha = 0.48132$. The dispersion and double refraction are high, the latter being exceeded only by that of calomel.

L. J. S.

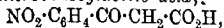
Gossypol, the Toxic Principle of Cotton Seed. FRANK E. CARRUTH (*J. Amer. Chem. Soc.*, 1918, 40, 647—663).—Gossypol is a colouring matter of phenolic nature occurring in glands in the seeds and in all parts of the cotton plant except the woody tissues. It is the toxic substance of cotton seed (compare A., 1917, i, 719). It may be precipitated as a compound with acetic acid or aniline by adding these agents to ethereal extracts of cotton seed. The first compound is decomposed by dissolving in ether, mixing with water, and distilling the solvent, when free gossypol separates on the surface, and the aniline salt is decomposed by hot alcoholic potassium hydroxide, the solution being then submitted to a current of steam and finally acidified.

Present analyses of gossypol, and molecular weight determinations, agree with the formula $C_{30}H_{28}O_8$ or $C_{30}H_{30}O_8$. The compound with acetic acid (1 mol.) corresponds with Marchlewski's gossypol (A., 1899, i, 821). A similar unimolecular compound with acetone, a tetra- or penta-acetate and -benzoate, a very sparingly soluble, orange-yellow aniline salt (2 mols. to $5NH_2Ph$), and some metallic salts are described.

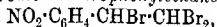
When heated at $186-190^\circ$, gossypol decomposes into a black mass, from which ether extracts a sparingly soluble, intensely yellow substance, m. p. $246-248^\circ$, termed B-gossypol. It is much less toxic than gossypol. Fusion with alkali hydroxide, followed by acidification in the presence of sodium hyposulphite (to prevent oxidation), gives a white product, C-gossypol. Cotton-seed meal, obtained by cooking the seeds for the oil, does not contain much gossypol as such, but D-gossypol (*loc. cit.*) instead. All four products behave alike in giving blood-red solutions in concentrated sulphuric acid and blue colorations when their alkaline solutions are exposed to the air. [See also *J. Soc. Chem. Ind.*, 319A.]

J. C. W.

o-Bromo-*m*-nitrostyrene has m. p. 76—77°, and not 59° as previously given (*loc. cit.*), and during its formation from $\alpha\beta$ -dibromo-*m*-nitrophenylpropionic acid there is produced at the same time some *m*-nitrobenzoylacetic acid,



m. p. 150°. The bromonitrostyrene on bromination in chloroform solution yielded *tribromo-m-nitrophenylethane*,



m. p. 56—87°.

W. G.

Preparation of Methyl *o*-Acetoxybenzoate. L. THORP (U.S. Pat. 1255950).—Methyl salicylate is heated with acetic anhydride in the presence of alkali acetate for ten to twenty hours at 90—100°, then alcohol is added, followed by water until a turbidity is produced, and, after cooling, the ester is collected.

A. S.

Normal Ammonium Salts of Organic Acids and their Substituted Derivatives. VII. LE ROY McMASTER and LETA WRIGHT (*J. Amer. Chem. Soc.*, 1918, **40**, 683—693. Compare A., 1913, i, 248, 444; 1914, i, 481, 1122; 1915, i, 958; 1916, i, 707).—An account of several more ammonium salts, prepared by the action of ammonia gas on the acids in anhydrous solvents.

The *2-hydroxy-m-toluate*, *4-hydroxy-m-toluate*, and *3-hydroxy-p-toluate* crystallise in cotton-like masses, and are non-hygroscopic and comparatively stable; the *2:4-dihydroxybenzoate* is pale pink, and the *2:5-dihydroxybenzoate* is white; the *2:4-dinitrobenzoate* is insoluble in most organic media, except methyl alcohol; the *o*-, *m*-, and *p*-nitrocinnamates are not hygroscopic and only sparingly soluble in water; the α - and β -*naphthoates* begin to decompose at 50°. The *m*-nitrobenzenesulphonate; the *m*-aminobenzenesulphonate, large, dark red plates; the *o*-naphthylamine-4-sulphonate, red and blue fluorescence in water; and the α -naphthol-4- and -5-sulphonates, unstable, brown powders, are described. The *benzilate* forms yellow granules; the *oxanilate* crystallises in slender needles, and the *phenylpropiolate* is a white powder.

J. C. W.

Preparation of Derivatives [Esters] of *iso*Valeric Acid. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (Brit. Pat. 113983).—The esters are prepared by the interaction of hydroxy-fatty acids (for example, glycollic and lactic acids or acids containing an aryl group, such as mandelic acid) and *iso*valeric acid, halogen-*iso*valeric acids, especially α -bromo-*iso*valeric acid, *iso*valeric anhydride, or *iso*valeryl chloride; or of *iso*valerates and the halogen fatty acids or their salts. They may be neutralised with inorganic or organic bases. The preparation of *iso*valerylmandelic [*iso*valeryloxyphenylacetic] acid, m. p. about 71°, both from *iso*valeryl chloride and from *iso*valeric acid, and of its calcium salt and its quinine salt,

m. p. 140°, of its α -bromo-derivative and of isovalerylglycollic [isovaleryloxyacetic] acid, m. p. 46—47°, both from glycollic acid and from sodium chloroacetate, is described.

A. S.

Preparation of an ω -Dihalogeno-*p*-toluoyl-*o*-benzoic Acid. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 297018; from *Chem. Zentr.*, 1917, i, 715—716).—When 2-*p*-toluoylbenzoic acid is treated with bromine at a high temperature, it is smoothly converted into 2- ω -dibromo-*p*-toluoylbenzoic acid (4-dibromomethyl-2'-carboxybenzophenone), a white powder, valuable as a source of anthraquinone derivatives, which changes into 4-aldehydro-2'-carboxybenzophenone [2-*p*-aldehydöbenzoylbenzoic acid] on heating with dilute alkali hydroxides.

J. C. W.

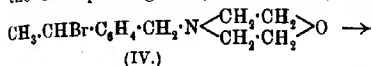
The Phenylsuccinic Acid Series. VI. Racemisation Phenomena Observed during the Investigation of the Optically Active Phenyl- and Diphenyl-succinic Acids and their Derivatives. HENRY WREN (T., 1918, 113, 210—218).—Since the esters of *r*-diphenylsuccinic acid are convertible into the esters of the *meso*-acid (this vol., i, 17), the same should be true of the optically active esters. The truth of this has been experimentally proved by the conversion of methyl and ethyl *l*-diphenylsuccinates into the *meso*-compounds by treatment with solutions of the appropriate sodium alkylloxides, and of ethyl *d*- and methyl *l*-diphenylsuccinates into *meso*-esters during partial hydrolysis.

It appears, therefore, that the considerable racemisation which occurs during the hydrolysis of these esters (A., 1915, i, 1061) is mainly due to rearrangement of the esters themselves, and not of the free acids. In this connexion, the more soluble *d*-phenylsuccinates have now been examined. The active methyl and ethyl esters are found to be rapidly and completely racemised by treatment with solutions of the alkylloxides, whilst the free *l*-phenylsuccinic acid is not appreciably affected. The portion of active ester which escapes hydrolysis when submitted to the action of insufficient potassium hydroxide dissolved in slightly diluted alcohol is also extensively racemised. Water has an influence on the extent of the racemisation, for the acid formed by complete hydrolysis with aqueous-alcoholic potassium hydroxide has a much higher rotation the greater the proportion of water in the agent.

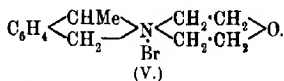
The tendency in recent years is to explain racemisation in the case of such esters on the basis of keto-enol desmotropy (see Frankland, T., 1913, 103, 725). No direct evidence of the usual kind has been obtained in the present case of the formation of sodium enolates, but, inasmuch as the strength of the alkali would have an influence on the extent of the enolisation, it is interesting to record that tetramethylammonium hydroxide causes even more complete racemisation of methyl *d*-phenylsuccinate than potassium hydroxide.

J. C. W.

ing tetrahydroisoquinoline, $\beta\beta'$ -di-iodoethyl ether, and 10% aqueous sodium hydroxide. It is a pale yellow, crystalline salt, m. p. 214—215°, and the corresponding *platinichloride* has m. p. 230°. When the iodide is converted into the hydroxide and this is distilled under reduced pressure, the main product is 1-*o*-vinylbenzylmorpholine, $\text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{O}$, which boils at 138—143°/6 mm., with partial polymerisation, and forms a *hydrochloride*, m. p. 211°, a *platinichloride*, red needles, m. p. 186°, a *picrate*, m. p. 164°, and a *methiodide*, m. p. 155—156°. The base combines with hydrogen bromide in concentrated solutions, forming an oily bromide (IV), which soon changes into the stable *quaternary bromide* (V), this having m. p. 213—215°, and yielding the corresponding red *platinichloride*, m. p. 220—223°. It may



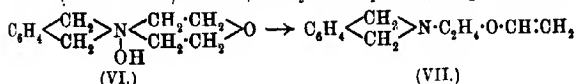
(IV.)



(V.)

also be reduced to 1-*o*-ethylbenzylmorpholine, a viscous oil, b. p. 138—140°/11 mm. (*picrate*, m. p. 142°; *platinichloride*, m. p. 189°), which reacts with cyanogen bromide to form *o*-ethylbenzyl bromide (A., 1917, i, 259). These reactions of the base are sufficient evidence that it is 1-*o*-vinylbenzylmorpholine; in other words, that it is the tetrahydroisoquinoline ring, and not the morpholine ring, which is ruptured when the quaternary ammonium hydroxide is heated.

For a comparison between the morpholine and dihydroisoindole systems, morpholine, *o*-xylylene dibromide, and 10% sodium hydroxide are warmed together, the quaternary ammonium bromide so formed is converted into the hydroxide (VI) (*platinichloride*, m. p. 225°; *aurichloride*, m. p. 147°), and this is distilled. The chief product is 2- β -vinyl α -ethyl dihydroisoindole (VII), which has b. p. 176—180°/12 mm., and yields a *picrate*, m. p. 105°, and



(VI.)

(VII.)

a *methiodide*, m. p. 129°. Consequently, the morpholine ring is the weaker in this case.

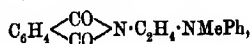
J. C. W.

Bromoalkylated Aromatic Amines. II. J. VON BRAUN, K. HEIDER, and E. MÜLLER (*Ber.*, 1918, 51, 273—282. Compare this vol., i, 107).—Some further reactions of methyl- β -bromoethylaniline are described, as well as the application of other secondary amines and ethylene dihaloids to the production of similar bromoalkylated bases.

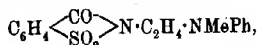
When methyl- β -bromoethylaniline is heated with formaldehyde and hydrobromic acid, it yields *dimethyldi- β -bromoethyl diamino-*

diphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{C}_2\text{H}_4\text{Br})_2$, which crystallises in colourless leaflets, m. p. 115—116°. If hydrochloric acid is used, the bromine is replaced and *dimethyldi-β-chloroethyl-diaminodi-phenylmethane*, m. p. 97—98° (*picrate*, m. p. 147°) is formed.

With potassium phthalimide at 145—150°, the base reacts vigorously, forming *methyl-β-phthalimidoethyl-aniline*,



in canary-yellow, glistening leaflets, m. p. 109°; *methiodide*, m. p. 165°. The potassium salt of "saccharin" yields the corresponding *β-benzoic-sulphimidoethyl-methylaniline*,



as a pale yellow, glistening mass, m. p. 115°, which forms an extremely bitter *methiodide*, m. p. 150°, and a *p-nitroso-compound*, a green powder, m. p. 190°, from which the *p-amino-derivative*,

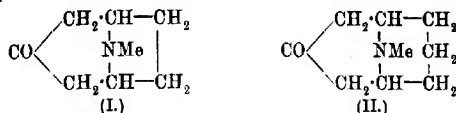
$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{C}_2\text{H}_4 \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \\ \diagdown \quad \diagup \\ \text{SO}_2 \end{array}$, may be obtained as a reddish-yellow powder, m. p. 111—112°. The "saccharin" derivative yields a flocculent diphenylmethane compound when heated with formaldehyde in the usual way. The hydrol obtained on oxidation with lead peroxide has a pure green colour in acid solutions, instead of the usual blue. To decide whether this difference is characteristic of the benzoic-sulphimide group, a number of typical dyes (not described) have been prepared with this *tert.* amine instead of a simple dialkylaniline, and in only one other case has an abnormally coloured product been obtained, namely, the compound related to methylene-blue, which is dark green.

Methylaniline reacts with *s*-chlorobromoethane under the conditions suitable for the production of methyl-β-bromoethyl-aniline to form a mixture of this with methyl-β-chloroethyl-aniline in almost equivalent quantities, having b. p. 116—120°/3 mm.

Ethylaniline and ethylene dibromide yield a mixture of diphenyl-diethylethylenediamine, $\text{C}_2\text{H}_4(\text{NEtPh})_2$, b. p. 223°/16 mm., and β-bromodiethylaniline, $\text{NEtPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$. The latter is a pale yellow oil, b. p. 151—154°/15 mm., which forms a *picrate*, m. p. 95°, and resembles methyl-β-bromoethyl-aniline in all its activities. For example, it reacts with sodium to give *diphenyldiethyltetramethylenediamine*, $\text{C}_4\text{H}_8(\text{NEtPh})_2$, b. p. 234—236°/12 mm.; *picrate*, m. p. 190°.

Methyl-*o*-toluidine and a large excess of ethylene dibromide, after heating for twenty-four hours, give a mixture of bases which are divided by distillation into (1) unchanged base, 20% of the weight of the base, (2) a fraction with b. p. 100—190°/6 mm., 40% and (3) a fraction with b. p. about 200°/6 mm., 48%. The second fraction is freed from unchanged base by converting this into its nitroso-compound, and then yields on redistillation *methyl-β-bromoethyl-*o*-toluidine*, b. p. 118—120°/5 mm., which forms a *picrate*

Analogues of Atropine and Homatropine. LOUIS F. WERNER (*J. Amer. Chem. Soc.*, 1918, **40**, 669—674).—When tropinone (I) is reduced by means of hydriodic acid, or electrolytically, it yields tropine, the tropate and mandelate of which are the well-known mydriatics atropine and homatropine. If reduced by means of sodium and alcohol, however, it gives ψ -tropine, the hydroxy-acid esters of which are not physiologically active. The alkaloid of the pomegranate, ψ -pelletierine (II), is a homologue of tropinone, and this also gives two isomerides on reduction.



When treated with sodium and alcohol, it yields the alkamine, methylgranatoline (Ciamician and Silber, A., 1894, i, 154); the *hydrobromide* of the *tropate* of this, m. p. 220°, and the *hydrobromide* of the *mandelate* are powerful mydriatics. Reduction with hydriodic acid and zinc dust at 0° gives *isomethylgranatoline*, m. p. 65°; the *tropate hydrobromide*, m. p. 233°; and *mandelate hydrobromide*, m. p. 229°, of this are inactive. Compared with the tropines, therefore, the products formed by like methods of reduction give esters of opposite physiological effects. J. C. W.

Preparation of Homologues of Emetine. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 301498; from *Chem. Zentr.*, 1918, i, 53).—Cephaeline is converted into its ethyl, propyl, and *benzyl* ethers. (Compare Karrer, A., 1916, i, 833, and Meader, *ibid.*, 834.) J. C. W.

The supposed Formation of Ergotoxine Ethyl Ester from Ergotinine. A Correction. GEORGE BARGER and ARTHUR JAMES EWINS (T., 1918, **113**, 235—238).—The phosphate obtained by boiling ergotinine in alcoholic solution with phosphoric acid is the salt of ergotoxine itself and not of its ethyl ester, as was originally supposed (T., 1910, **97**, 284). From the results of Zeisel determinations, the authors are inclined to believe that ergotoxine and ergotinine contain one *N*-methyl group, but no methoxy-group. J. C. W.

The Alkaloids of Ipecacuanha. III. FRANK LEE PYMAN (T., 1918, **113**, 222—234. Compare A., 1917, i, 410).—In the last communication it was shown that *O*-methylpsychotrine yields emetine and *isoemetine* on reduction. The formation of the latter isomeride was demonstrated by the isolation of its previously known benzoyl derivative; it is now confirmed by the actual separation of the base itself, some characteristic salts of which are described. On oxidation, *isoemetine*, like emetine, may be converted into *O*-methylpsychotrine or rubremetine, which shows

that the two bases are stereoisomerides. Equilibrium between them could not be established, however, by boiling with sodium and amyl alcohol. *iso*Emetine is rather less than half as toxic as emetine.

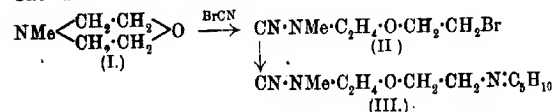
Psychotrine itself yields cephaeline and *iso*cephaeline on reduction, and, as might be expected, the latter may be converted into *iso*emetine by methylation. *iso*Emetine may be transformed under suitable conditions into *N*-methyl*iso*emetine, and this may also be formed by methylating *N*-methyl*iso*cephaeline (T., 1914, 107, 1624).

N-Methyl*iso*emetine has also been completely methylated, the product being a mixture of a crystalline and an amorphous methiodide, apparently stereoisomerides, since they yield the same *N*-methyl*iso*emetine methine when the methohydroxides are heated. In the same way, emetine itself forms two *N*-methylemetine methiodides, which yield the same methine.

For details, the original should be consulted, where a chart showing the relationships between the ipecacuanha alkaloids, established experimentally by the author, will be found. J. C. W.

Relative Stability of Cyclic Bases. VI. The Morpholine Ring. J. VON BRAUN and Z. KÖHLER (*Ber.*, 1918, 51, 255—265. Compare this vol., i, 185).—The authors have established the order of stability of a number of cyclic bases under the disruptive influence of cyanogen bromide and in the Hofmann reaction. It is now found that the morpholine system is to be placed along with tetrahydro*iso*quinoline and dihydro*iso*indole among the bases which are most easily ruptured by cyanogen bromide, and between these two in stability during the Hofmann reaction.

1-Methylmorpholine (I) (Knorr, A., 1898, i, 602) reacts very vigorously with cyanogen bromide diluted with ether, giving a crystalline precipitate of the hydrobromide of the base mixed with a trace of an undefined compound, $C_5H_{12}ON_3$, and a solution which contains an unstable oil (II). This condenses with piperidine to form β -cyanomethylaminoethyl β -1-piperidinoethyl ether (III), b. p. 170—175°/30 mm., which forms a *platinichloride*, stout, red, tablets, m. p. 166°, and a *picrate*, m. p. 139—140°. The main reactions are therefore represented by the scheme:



In order to compare the stability of the morpholine ring with the tetrahydro*iso*quinoline system under the conditions of the Hofmann reaction, a compound with a nitrogen atom common to both rings has been prepared. This is the *quaternary ammonium*

iodide, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C}_4\text{H}_8 \cdot \text{CH}_2 \end{array} \cdot \text{N}^+ \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \cdot \text{O}^-$, which is obtained by mix-

alene, or the substituted benzoylamino-analogues, in the presence of Turkey-red oil, or such substances, with or without a substrate.

The 8-benzoylamino- β -naphthols employed are mostly colourless, crystalline compounds. The following are mentioned: 8-benzoylamino- β -naphthol, m. p. 208—209°; 8-*o*-chlorobenzoylamino- β -naphthol, m. p. 158—160°; 8-*p*-chlorobenzoylamino- β -naphthol, m. p. 230—231°; 8-*op*-dichlorobenzoylamino- β -naphthol, m. p. 186—187°; 8-2':6'-dichlorobenzoylamino- β -naphthol, m. p. 230—232°; 8-*o*-nitrobenzoylamino- β -naphthol, m. p. 227—228°; 8-*m*-nitrobenzoylamino- β -naphthol, m. p. 204—205°; 8-*p*-nitrobenzoylamino- β -naphthol, m. p. 255—260° (decomp.). J. C. W.

Preparation of Acid Mono-azo-dyes for Wool. FARBEN-FABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296964; from *Chem. Zentr.*, 1917, i, 717).—Good dyes which colour wool yellow to bluish-red or brown shades in acid baths are obtained by coupling pyrazolone-, methylketol-, α - or β -naphthol-, or 8-acylamino- α -naphthol-sulphonic acids with diazotised phenylenediamines of the type $\text{NH}_2\text{R}'\text{NRR}'$, where R = alkyl or aryl, R' = an aromatic acyl group, such as Bz or $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$, and R' = the benzene nucleus or a homologue or substituted nucleus. The necessary bases are obtained by treating alkylated or arylated anilines with benzoyl chloride or substituted benzoyl chlorides, nitrating the products, and then reducing the nitro-compounds.

Thus, ethylaniline, after benzylation, nitration, and reduction, yields benzoylethyl-*p*-phenylenediamine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NEtBz}$, m. p. 114°, and methylaniline gives benzoylmethyl-*p*-phenylenediamine, m. p. 143°. Benzoylethyl-*m*-toluidine yields benzoylethyltolylene-2:5-diamine, m. p. 140°; benzoylethyl-*p*-xylylene yields benzoylethyl-*p*-xylylene-2:5-diamine, $\text{NH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CMe} \\ \text{CMe}\cdot\text{CH} \end{smallmatrix}\cdot\text{C}\cdot\text{NEtBz}$, m. p. 134°; benzoylmethyl-*o*-toluidine gives benzoylmethyltolylene-2:4-diamine, m. p. 167°; 2'-chlorobenzoylethylaniline gives 2'-chlorobenzoylethyl-*p*-phenylenediamine, m. p. 135°; and 4-nitrodiphenylamine yields benzoylphenyl-*p*-phenylenediamine, m. p. 178°.

J. C. W.

Preparation of Yeast-nucleic Acid. EMIL J. BAUMANN (*Proc. Amer. Soc. Biol. Chem.*, 1917, xiv.-xv.; *J. Biol. Chem.*, 1918, **33**).—Fresh brewer's yeast is diluted with water and treated with sodium hydroxide solution (100 grams of alkali per kilo. of yeast) in the cold, which separates the nucleoprotein into protein and nucleic acid. Since nucleic acid is soluble in dilute acetic acid, the solution is now partly neutralised with hydrochloric acid and then made acid with acetic acid. The precipitated proteins are removed by filtration and the nucleic acid in the filtrate precipitated by the addition of 5% magnesium sulphate solution and enough hydrochloric acid to cause the separation of the flocculent precipitate. The yield of dry mono-magnesium nucleate is 4 to 7½ grams per kilo. of yeast

H. W. B.

Nucleic Acid of the Lymph Corpuscle. R. NAKASAKO (*A. C. James Res. Lab., Bull.*, 1917, No. 3; from *Physiol. Abstr.*, 1918, 3, 4—5).—The nucleic acid was prepared from lymph glands by a modification of Kossel's method. It closely resembles the thymus acid, and to it the author assigns the formula $C_{41}H_{55-64}O_{25}N_{14}P_4$. Amongst the products of hydrolysis, xanthine, hypoxanthine, guanine, adenine, thymine, and a compound containing either of the groups $CH_3 \cdot CO \cdot C$ and $CH_3 \cdot CH(OH) \cdot C$ were identified. The existence of a carbohydrate is uncertain.

W. G.

Effect of Potassium Bromate on Enzyme Action. I. S. FALK and C.-E. A. WINSLOW (*J. Biol. Chem.*, 1918, 33, 453—462).—Potassium bromate exerts a slight stimulating action on trypsin and pancreatin when it is present in concentrations of 1 part in 100,000 to 1 part in 250,000. With higher concentrations, the proteolytic action is depressed.

H. W. B.

Action of Ammonium Compounds on Ptyalin. ELBERT W. ROCKWOOD (*Proc. Amer. Soc. Biol. Chem.*, 1917, ix-x; *J. Biol. Chem.*, 1918, 33).—Ammonium salts of inorganic and organic acids increase the activity of ptyalin. In general, the ammonium salts of the strong acids have a greater activating effect than those of the weak acids. Ammonium oxalate is an exception, having little or no action.

H. W. B.

The Action of Acids on Ricinus Lipase and the Reaction of the Substratum. G. KITA (*J. Chem. Ind., Tokyo*, 1918, 21, 1—4).—Green and Hoyer have shown that acids have a powerful activating influence on the lipase of castor beans, and that the activated lipase exerts its specific activity in neutral media. Further, lipase which has been rendered active by treatment with acids and thoroughly washed has a more powerful action in faintly acid media than in neutral. The author has found that the activated lipase, which is extremely unstable in presence of acids, becomes comparatively far more permanent in presence of the oil to be hydrolysed. Armstrong overlooked this fact, and considered that the acid played some other part than the liberation of the zymogen, because the quantity of acid which is most favourable to fat hydrolysis was capable under the same conditions of destroying the lipase of de-fatted castor beans. The author considers that, although the activated lipase is again rendered inactive by acids, the simultaneous presence of fat is capable of exerting a protective action on the lipase in the hydrolysis of fats.

J. F. B.

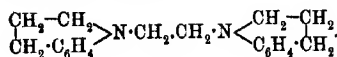
The Action of Aldehydes on Urease. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, 85, 358—364).—Aldehydes inhibit the action of urease. The cyanohydrin of acetaldehyde, however (but not that of benzaldehyde) accelerates the action.

S. B. S.

m. p. 90°, and reacts with trimethylamine to give the *quaternary bromide*, $C_6H_4Me \cdot NMe \cdot CH_2 \cdot CH_2 \cdot NMe_3Br$, glistening leaflets, m. p. 173—174°. The third fraction is mixed with trimethylamine to remove any bromoalkylated base as the foregoing salt, and then *di-o-tolylidimethylethylenediamine*, $C_6H_4(NMe \cdot C_6H_4Me)_2$, is recovered as a hard mass, m. p. 46—47°, b. p. 199—201°/6 mm., which forms a *picrate*, m. p. 178°, and a *dibromide*, m. p. 88°.

Methyl- α -naphthylamine also yields a bromoalkylated base when heated with ethylene dibromide, but it decomposes on distillation. The parent substance is obtained as follows. The dimethyl- α -naphthylamine of commerce is warmed with cyanogen bromide, which yields α -naphthyltrimethylammonium bromide, m. p. 160°, insoluble in ether, and *cyanomethyl- α -naphthylamine*, $C_{10}H_7 \cdot NMe \cdot CN$, a yellow oil, b. p. 189—191°/5 mm., soluble in ether, and the latter is hydrolysed to methyl- α -naphthylamine by boiling with 20% hydrochloric acid.

Tetrahydroquinoline and ethylene dibromide yield, chiefly, crystalline *s:l:1-ditetrahydroquinolyethane*,



J. C. W.

Ethylisopropylbarbituric Acid. L. THORP (U.S. Pat. 1255951).

—Ethylisopropylbarbituric acid, prepared by the usual methods, forms snow-white crystals (from water), m. p. 197—198°, has a faint, bitter taste, and is readily soluble in alcohol or ether. The acid and its alkali salts, which are readily soluble in water, possess marked hypnotic and sedative powers, and are relatively devoid of toxic action.

A. S.

Compounds derived from Diallylbarbituric Acid and Alkaloids of the Morphine Series and Process of making same.

SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1255423, 1918; from *J. Soc. Chem. Ind.*, 1918, **37**, 193A. Compare A., 1917, i, 664).—The compound formed by diallylbarbituric acid and ethylmorphine is a white, crystalline substance, m. p. 285°. The compounds generally are easily soluble in hot water, methyl or ethyl alcohol, acetone, or ethyl acetate, but insoluble in light petroleum.

H. M. D.

Preparation of Phenylethylbarbituric Acid. MARY RISING and JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1918, **40**, 723—730).

—Some practical notes on the preparation of the necessary intermediate compounds and on the final stages in the synthesis of phenylethylbarbituric acid. This compound, which was introduced as a specific in cases of epilepsy under the name “luminal,” is officially designated “phenylbarbital” in America, as veronal is termed “barbital.” [See, further, *J. Soc. Chem. Ind.*, 322A.]

J. C. W.

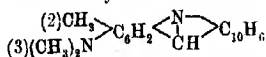
Preparation of Nitrogenous Vat Dyes of the Anthracene Series. CHEMISCHE FABRIK GRIESHEIM ELEKTRO (D.R.-P., 301554; from *Chem. Zentr.*, 1918, i, 150).—The yellow vat dye obtained by the action of concentrated alcoholic alkali hydroxide on pyrazole-anthrone (A., 1913, i, 533) forms alkali salts which react with the usual alkylating agents. The alkyl derivatives so formed are much deeper in colour than the parent dye; for example, the *benzyl* compound is scarlet, and the *ethyl* derivative, Bordeaux-red.

J. C. W.

Halogenated Dyes of the Acridine Series. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (U.S. Pat. 1255739).—A new acridine dye obtained by heating chloroformyl-*m*-phenylenediamine ($\text{NH}_2 \cdot \text{NH} \cdot \text{CHO} : \text{Cl} = 1 : 3 : 6$) with *m*-phenylenedimethyl-diamine hydrochloride, is a brownish-black powder which dyes leather reddish-yellow. The patent covers derivatives of dyes of the general formula $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \langle \begin{smallmatrix} \text{N} \\ | \\ \text{CH} \end{smallmatrix} \rangle \text{C}_6\text{H}_3 \cdot \text{NR}_1\text{R}_2$, in which R_1 and R_2 represent univalent substituents, including hydrogen, and one or more hydrogen atoms of the benzene nuclei have been displaced by halogen.

A. S.

Acridine Dyes of the Benzene-naphthalene Series. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (U.S. Pat. 1255740).—A new acridine dye of the formula:



is a reddish-brown powder, which dyes leather in deep orange-yellow shades. The patent covers dyes of the general formula $\text{R}_2\text{R}_1\text{N} \cdot \text{C}_6\text{H}_4 \langle \begin{smallmatrix} \text{N} \\ | \\ \text{CH} \end{smallmatrix} \rangle \text{C}_{10}\text{H}_6$, obtained by heating a formyl derivative of β -naphthylamine with a salt of a *m*-diamine of the benzene series.

A. S.

Preparation of Condensation Products of Isatin and Ketones. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P., 301591; from *Chem. Zentr.*, 1918, i, 148—149).—Condensation products, of unexplained nature, are obtained by mixing acetophenone or its derivatives with isatin and ammonia solution. Acetophenone itself gives a pale yellow product, $\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}$ [η , m. p. 152—153°; *p*-tolyl methyl ketone yields a white product, m. p. 165—167°; deoxybenzoin forms a product, m. p. 147°; and the product from 3-nitro-4-hydroxyacetophenone forms yellow crystals, m. p. 191°.

J. C. W.

Preparation of Mono-azo-dyes suitable for Pigment Manufacture. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 296991; from *Chem. Zentr.*, 1917, i, 718).—Diazotised 1-amino-anthraquinone is coupled with 1-benzoylamino-7-hydroxynaphth-

Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON HEYDEN, AKT.-GES. (D.R.P., 296940; with 261825 and 269255, an addition to 254421; from *Chem. Zentr.*, 1917, i, 715. Compare A., 1913, i, 416, 1122; 1914, i, 217).—Nitro-derivatives of aromatic stibinic acids are prepared by treating diazotised nitroamines with antimonites or antimonious acid, in acid or neutral solutions, at low temperatures. Antimony trioxide dissolved in such an acid as tartaric acid is recommended, and copper powder is often useful as a catalyst. 2-Nitro- and 2:4-dinitro-phenylstibinic acids are brown powders which explode on heating. 3-Nitro-panilinoarsinic acid yields 2-nitro-4-arsinophenylstibinic acid, $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{SbO}_3\text{H}_2$, which is a similar brown powder.

J. C. W.

Physiological Chemistry.

The Oxygen and Carbon Dioxide Tension in the Blood of the Pulmonary Artery and the Measurement of the Minute Volume of the Heart. L. S. FRIDRICIA (*Biochem. Zeitsch.*, 1918, 85, 307—357).—The method of measurement employed by the author is described in detail. It is based on the use of a spirometer constructed by Krogh on the principle of the aeroplethysmograph. It was found that the tensions of oxygen and carbon dioxide in pulmonary blood are not constant in the same individual when in a state of rest. The average values for three persons were 40.7, 44.5, and 35.1 mm. for oxygen and 45.2, 46.3, and 45.2 mm. for carbon dioxide. There are wider variations, therefore, in the oxygen than in the carbon dioxide tensions. During muscular work (200 kg./m. per minute), the ratios of the tensions to the tensions found for the same individual when at rest were for oxygen 35.2:44.5, and for carbon dioxide 55.2:46.3. The minute volume of the heart was estimated by the methods of Krogh and Lindhard and of Fick, and the two were found to give results which were satisfactorily concordant.

S. B. S.

Comparison of the Dextrose and Cholesterol Content of the Blood. F. H. MCCRUDDEN and C. S. SARGENT (*J. Biol. Chem.*, 1918, 33, 387—389).—The amounts of dextrose and of cholesterol in the blood in various diseases do not show any kind of parallelism. The association of hyperglycæmia and hypercholesterolemia in diabetes (Bloor, Joslin, and Hornor, A., 1916, i, 776) is therefore probably due to an indirect physiological relationship.

H. W. B.

Fatty Acids in Human Blood in Normal and Pathological Conditions. FRANK A. CSOKA (*J. Biol. Chem.*, 1918, 33, 401—409. Compare A., 1916, ii, 349).—The method

previously described for the estimation of fatty acids in faeces (Gephart and Csonka, A., 1915, ii, 74) can be applied in the case of blood, using 5 c.c. of oxalated blood, and the author's saponification and extraction flask (*loc. cit.*). For the estimation of the unsaturated fatty acids, about 100 c.c. of blood are extracted with alcohol and ether, and the extract saponified by the Gephart and Csonka method. The mixed fatty acids are converted into their lead soaps, which are then extracted with ether, which dissolves the lead soaps of the unsaturated fatty acids. The free acids are liberated from the soaps by hydrochloric acid, and, after weighing, the iodine numbers are determined according to Hübl.

The blood of normal individuals contains about 0.14 gram of unsaturated fatty acids per 100 c.c., with an average iodine number of 87.5. The iodine number varies from 76 to 105, thus indicating the presence, in addition to oleic acid, of other both higher and lower unsaturated fatty acids in small amounts. In normal human blood, about one-half of the total fatty acids are unsaturated. In pathological conditions, there is generally a higher proportion of unsaturated fatty acids with higher iodine values, especially in cases where the hæmoglobin content of the blood is low. In such cases, the smaller number of red corpuscles present in the blood reduces the amount of unsaturated fatty acid which can be utilised for metabolic purposes, and this results in an accumulation of unsaturated fatty acids in the blood (compare Bloor, A., 1916, i, 450).

H. W. B.

Adsorption Phenomena in Coagulation. G. H. A. CLOWES (*Proc. Amer. Soc. Biol. Chem.*, 1917, xx; *J. Biol. Chem.*, 1918, 33).—The author has determined the effect on the coagulation of blood of the addition of precipitated or colloidal barium sulphate, calcium oxalate, etc., which adsorb prothrombin. The adsorption is proportional to the degree of dispersion of the adsorbent and depends also on the presence of unsaturated lipoids like kephalin. Apparently the physical quality and speed of formation of the blood clot depend on the degree of dispersion of the reacting colloids and on their initial and final concentrations.

H. W. B.

Relation between Phosphorus Metabolism and the Secretion of Milk-fat. EDWARD B. MEIGS and N. R. BLATHERWICK (*Proc. Amer. Soc. Biol. Chem.*, 1917, iv—v; *J. Biol. Chem.*, 1918, 33).—Experiments on cows are described in which the distribution of phosphorus in the blood is determined before entering and after leaving the mammary gland. When the cow is disturbed by the operative procedure, the lipid phosphorus in the blood remains unaltered, but when the cow is quiet, a diminution in the lipid phosphorus occurs during the passage of the blood through the active gland. In all cases, an increase in the inorganic phosphate in the blood coming from the gland is observed.

The authors consider that the results show that the precursor

in the blood of both milk fat and milk phosphorus is either lecithin or a related compound. The ratio phosphorus:fat in lecithin is about 1:18, whereas it is about 1:50 in milk. Hence relatively more phosphorus is supplied to the gland than is required for the milk, and the excess is returned to the blood as inorganic phosphate.

H. W. B.

Metabolism of α -Carbamidoisobutylacetic Acid. ALICE ROHDE (*Proc. Amer. Soc. Biol. Chem.*, 1917, xii; *J. Biol. Chem.*, 1918, **33**. Compare A., 1917, ii, 344).—The intravenous injection of α -carbamidoisobutylacetic acid in saline solution into a cat is followed by the elimination of a considerable proportion of the acid in the urine. The acid is identified by the method previously described in the case of phenylalanine-carbamido-acid (*loc. cit.*).

H. W. B.

Endogenous Uric Acid Metabolism. HOWARD B. LEWIS, MAX S. DUNN, and E. A. DOTY (*Proc. Amer. Soc. Biol. Chem.*, 1917, xv—xvi; *J. Biol. Chem.*, 1918, **33**).—The authors describe the influence of the ingestion of proteins and various protein derivatives on the hourly elimination of uric acid in a subject on a purine-free low protein diet. Protein (egg-white, cheese) causes a slight rise, beginning the second hour after the meal and increasing to a maximum at the fourth hour. Ingestion of equivalent amounts of nitrogen in the form of glycine or alanine results in a sharp rise in the second hour, followed by a prompt return to the normal level. Administration of a second portion of glycine following the return to normal causes a like increase in the uric acid excretion. Aspartic and glutamic acids produce eliminations of uric acid of even greater magnitude. Neither urea nor ammonium chloride administered in amounts comparable to the amino-acids has any influence on the output of uric acid. The authors draw the conclusion that the rise in the excretion of uric acid following ingestion of protein food is not due mainly to the work of the digestive glands, but to stimulation of the cellular mechanism by the amino-acids liberated in the digestion of the protein. Creatinine excretion was not affected in any of the experiments.

H. W. B.

Role of some Inorganic Elements in Nutrition. LAFAYETTE B. MENDEL and THOMAS B. OSBORN (*Proc. Amer. Soc. Biol. Chem.*, 1917, iii; *J. Biol. Chem.*, 1918, **33**).—The essential factors of a successful dietary having now been ascertained, it has become possible to prepare rations in which the individual ions are excluded except for the unavoidable small amounts present in the products used to supply the water-soluble vitamins or found as impurities in the other ingredients of the food. Experiments with such diets demonstrate that calcium and phosphorus are needed in considerable amounts, for with only a trace of either of these elements in the diet, rats fail to grow and sooner or later decline.

On diets in which one of the elements magnesium, sodium, potassium, or chlorine are absent, growth continues at the normal rate. When both sodium and potassium are absent, growth does not occur.

H. W. B.

Formation of Structures Resembling Organic Growths by Electrolytic Action in Metals. R. S. LILLIE (*Biol. Bull.*, 1917, **33**, 135—186; from *Physiol. Abstr.*, 1918, **3**, 7—8).—A study of the conditions under which filaments, formed of ferri-cyanides of iron, zinc, copper, etc., are produced in mixtures of albumin and potassium ferrocyanide. Only those metals the ferri-cyanides of which form semipermeable membranes exhibit the phenomenon. The author suggests that in organic growth the essential structural condition is possibly the presence of semipermeable, and hence electrically polarised, partitions separating the living substance from its medium, and at which the process of electrolysis may take place.

W. G.

Differences in the Swelling of the Plasma Colloids as a Cause of the Invagination of the Gastrula and generally of the Curving and Folding of Layers of Cells. JOSEF SPEK (*Koll. Chem. Beihefte*, 1918, **9**, 259—399).—A paper, mainly of biological interest, in which an attempt is made to show that changes in the geometrical form of certain tissues are due to differences in the extent to which the colloidal constituents of the cells are swollen by the absorption of water. The degree of swelling is appreciably affected by the electrolytes present, and the results of some observations on the swelling of fibrin under the influence of solutions of acids and salts are recorded. These show that for salt concentrations which fall within the physiological range, the effect of the presence of acids is to increase considerably the degree of swelling of the plasma colloids.

H. M. D.

Autolysis. H. C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, 1917, xi; *J. Biol. Chem.*, 1918, **33**).—The autolysis of nervous tissue, like muscle and gland tissues, is accelerated by acids and inhibited by alkalis. Striated muscle autolyses more slowly than either cardiac or involuntary muscle. The accelerating action of inorganic hydrosols on the autolysis of liver described by Ascoli and Izar (*A.*, 1909, ii, 501) is not confirmed.

H. W. B.

Conjugation of Hippuric Acid. E. LACKNER, A. LEVINSON, and WITHROW MORSE (*Proc. Amer. Soc. Biol. Chem.*, 1917, xvi—xviii; *J. Biol. Chem.*, 1918, **33**).—After fatty degeneration of the liver has been produced in dogs by the subcutaneous injection of hydrazine, ingestion of sodium benzoate causes a diminished output of hippuric acid compared to that observed in the normal animal. Apparently the kidney is not affected by the hydrazine injection, and therefore the authors draw the conclusion that, normally, conjugation of hippuric acid occurs in the liver. These

results are confirmed by the following clinical observations. In normal children, ingestion of sodium benzoate produces an increased elimination of hippuric acid. A case of a child with diseased liver is described in which administration of sodium benzoate did not have any effect on the output of hippuric acid.

H. W. B.

Creatine Content of Skeletal Muscle in Degeneration following Denervation. E. P. CATHCART, P. S. HENDERSON, and D. NOËL PATON (*J. Physiol.*, 1918, 52, 70—74).—Up to the eleventh day after section of the nerve there is no distinct change, but after the fifteenth day, when the reaction of degeneration is well established, there is a steady and progressive decrease in the creatine content of muscle, becoming very pronounced (30—60%) between the third and fourth weeks.

G. B.

Guanidine Content of Muscle in Tetania Parathyreopriva. PEARL S. HENDERSON (*J. Physiol.*, 1918, 52, 1—5).—Removal of the parathyroids causes a fall in the total and in the free guanidine of muscle and a rise in the creatine content corresponding fairly closely with the fall in free guanidine. The fall in total guanidine is, however, so great that it may be correlated with the increase in blood and urine (compare Burns, A., 1916, i, 617).

G. B.

Cell Penetration by Acids. IV. Penetration of Phosphoric Acid. W. J. CROZIER (*J. Biol. Chem.*, 1918, 33, 463—470. Compare A., 1916, i, 694).—With mantle tissue of *Chromodoris*, the coagulating action of phosphoric acid is so pronounced that a relatively high concentration must be employed before there is marked acceleration in the speed with which the quantity of acid sufficient to react with the indicator is forced to diffuse into the tissue. The actual speed of protoplasmic penetration by phosphoric acid is probably much greater than its apparent magnitude.

H. W. B.

Catalase Content of *Ascaris suum*, with a Suggestion as to its Role in Protecting Parasites against the Digestive Enzymes of their Hosts. THOMAS BYRD MAGATH (*J. Biol. Chem.*, 1918, 33, 395—400).—The relative amounts of catalase contained in two or more tissues are estimated by measuring the volumes of oxygen evolved when equal weights of the tissues are placed in contact with excessive quantities of hydrogen peroxide. The apparatus employed is similar to that used for the estimation of urea by the hypobromite method; hydrogen peroxide is placed in the bottle together with a crucible containing the weighed tissue. The bottle is connected with a measuring burette and levelling tube filled with water. After the crucible has been upset, the oxygen evolved is readily measured and corrected for normal temperature and pressure.

The whole worm yields 15 c.c. of oxygen per gram, the body

wall 13 c.c., the body fluid 7 c.c., and the visceral organs 26 c.c. per gram. Whilst these amounts are small as compared with those obtained from free living animals, it is pointed out that if the catalase in the respective reproductive organs be taken as the unit, then the body wall of *Ascaris* contains three times as much catalase as the leg muscles of the frog. It is probable, therefore, that there is more than enough catalase in the body wall of this worm for its metabolic and locomotory functions, and it is possible that the excess is used to liberate oxygen for protecting the parasite against the digestive enzymes of its host (see Burge, A., 1915, i, 614).

H. W. B.

Food Fishes. Analysis of Twenty Common Food Fishes with Especial Reference to a Seasonal Variation in Composition. ERNEST D. CLARK and LLOYD H. ALMY (*J. Biol. Chem.*, 1918, 33, 483—498).—The authors have analysed the edible portions of various fishes at different periods of time. In the case of the shad, the spawning period is about two months, during which time the fish appear in the rivers in April and ascend to fresh-water, returning to the sea in June. The amount of fat in the edible portion of the fish diminishes from 14.4% before spawning to 2.95% afterwards. The shad, like the salmon, does not feed during the spawning migration, and doubtless some of the fat is consumed in the tissues to furnish the energy necessary for ascending the rivers, and the remainder is transferred to the roe and milt.

In most fishes, the fat content varies inversely as the water content, the proportion of fat-free solids remaining constant. The fish oils are fairly uniform, the constants being D_{20}^{25} 0.9220, n_D^{25} 1.4750, iodine number 110—130, and saponification number 180—190. The amounts of water-soluble nitrogen and coagulable nitrogen are also fairly constant for the same kind of fish taken at different times, whilst the amounts of these substances may be widely different for different species of fish.

H. W. B.

The Biochemistry of Certain Conditions of Oedema. I. Blood and Serum. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, 85, 365—405).—The investigations refer to certain cases of "oedema disease" observed chiefly in prisoners of war. The chief results were the following: Diminution in blood, especially in the plasma of fatty acids and lipoid phosphorus; hypoglycæmia, increase in acetone substances, residual nitrogen, ammonia, cholesterol, and acid-soluble phosphorus; small increase in sodium chloride. Diminution of iron and potassium; moderate hydræmia, but, with the exception of lymphocytosis, no marked abnormality in the formal elements of the blood, and other characters. The author discusses the clinical bearings of the results.

S. B. S.

The Part Played by an "Accessory Factor" in the Production of Experimental Rickets. EDWARD MELLANBY (*Proc. Physiol. Soc.*, 1918, xi—xii; *J. Physiol.*, 52).—Two diets,

(1) milk, rice, oatmeal, and sodium chloride, (2) milk and bread, produce rickets in puppies in the course of three to four months if the milk is kept below 200 c.c. per day. Rickets was prevented by extracts of meat, malt, and yeast, by butter, margarine, and cod-liver oil, but not by protein of meat, casein, linseed oil, or 10 grams of yeast per day. Hence it would appear that rickets is due to the lack of an accessory factor in the diet. G. B.

Degradation of Aliphatic Acids in the Animal Body. EMIL LENK (*Munch. Med. Woch.*, 1917, **64**, 1460; from *Chem. Zentr.*, 1918, i, 121).—The author has shown that acetoacetic acid may be oxidised to acetic acid by heating with acetic acid and permanganate (A., 1917, ii, 399), and believes that a similar degradation of the acid by the attack of oxidising agents on the ethylene linking (of the enolic modification) may proceed in the body. Other facts indicate that acetic acid may be formed in the body as the result of reduction, so the degradation of fatty acids, which is so complete that only traces of the higher members are ever found in normal urine, may be due to both processes. J. C. W.

Elimination of Taurine administered to Man. CARL L. A. SCHMIDT, EDWARD VON ADELUNG, and THOMAS WATSON (*J. Biol. Chem.*, 1918, **33**, 501—503).—The administration of from 3 to 10 grams of taurine subcutaneously, intravenously, or by the mouth is followed by an increased elimination of neutral sulphur in the urine. From 59 to 86% of the taurine sulphur is thus recoverable from the urine. Large doses of taurine administered to rabbits or to human subjects do not appear to produce any toxic effects. H. W. B.

The Character of the Toxic Action of Suprarenine [Adrenaline]. OSCAR LOEW (*Biochem. Zeitsch.*, 1918, **85**, 295—306).—When in the form of its salts in a neutral solution, adrenaline has only a very slightly toxic action. The free base, however, and its first red oxidation product is extremely toxic, and this action can be readily demonstrated on the nucleus of *Spirogyra*. The author ascribes the toxicity to the lability of the hydrogen ions in the molecule, which is specially marked in alkaline solution. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Nitrogen Content of Bacterial Cells. I. Method. HAROLD C. BRADLEY, and M. STARR NICHOLS (*J. Biol. Chem.*, 1918, **33**, 525—529).—The bacterium is grown on a solid medium and the culture then transferred by a glass spatula to a tared

cover-slip and dried at 37° in a desiccator to constant weight. The nitrogen is subsequently estimated by Folin's micro-method.

Employing quantities of about 5 mg. of dry bacteria for analysis, *B. diphtheriae* are found to contain about 8.4, and *B. hoffmanni* 9.6 per cent. of nitrogen. H. W. B.

The Bacterial Metabolism of Sulphur. II. Formation of Hydrogen Sulphide from certain Sulphur Compounds by Yeast-like Fungi. FRED W. TANNER (*J. Amer. Chem. Soc.*, 1918, 40, 663—669).—The growth of some thirty varieties of budding fungi, mainly yeast species, has been studied in culture media containing peptone, cystine, sodium thiosulphate, sulphate, and sulphite, potassium thiocyanate, thiocarbamide, sodium phenolsulphonate and taurocholate, or sulphur itself. All of them were found to produce hydrogen sulphide from cystine, but only eleven developed it from peptone; twenty-two varieties gave very positive results with the thiosulphate, and distinct lead paper reactions when grown with the sulphite, whilst ten reduced even the sulphate; about two-thirds produced hydrogen sulphide from free sulphur; sodium taurocholate was reduced by two varieties only, and the phenolsulphonate by *Mycoderma lactis* only, although growth was quite good on this substrate. *M. lactis* has the largest all-round reducing power. J. C. W.

Bactericidal Properties conferred on the Blood by Intravenous Injection of Diaminoacridine Sulphate. C. H. BROWNING and R. GALBRANSEN (*Proc. Roy. Soc.*, 1918, [B], 90, 136—144).—Attention is directed to the fact that certain acridine derivatives, unlike most other antiseptics, have a stronger bactericidal action in the presence than in the absence of serum, and, furthermore, that the toxic action increases progressively with time. Some experiments show that when diaminoacridine sulphate is injected into rabbits, their sera become bactericidal to *Staphylococcus aureus* and *B. coli*, even after heating at 56°. S. B. S.

Enzyme Formation. HANS EULER (*Biochem. Zeitsch.*, 1918, 85, 406—417).—Attention is directed to the fact that the formation of a ferment (invertase) in developing yeast is not necessarily parallel with the rate of growth. A series of experiments was carried out with culture media containing, in addition to sucrose and the necessary inorganic salts, the following substances as sources of nitrogen: glycine, glycine + cystine, glycine + tyrosine, asparagine, alanine, and yeast water. There was no marked difference in the rate of growth with different amino-acids, but it was less than that in yeast water. In yeast water, the rate of formation of invertase was greater than in presence of pure amino-acids, but here again there was no marked difference in the action of the individual acids. S. B. S.

Volutin and its Chemical Composition. M. A. VAN HEERWERDEN (*Folia Microbiologica. Nederl. Tydschr. voor Mikrobiologie*, 1917, 5, pp. 12; from *Chem. Zentr.*, 1918, i, 216).—If

organisms like *Ustilago maydis*, *Torula monosa*, lactose yeast, or *Saccharomyces cerevisiae* are cultivated on media which are free from phosphates, they do not develop volutin, but this immediately appears in the cells if the cultures are transferred to a phosphate mixture. A nucleic acid derivative is also extracted from ordinary cultures when the isolation of volutin is aimed at, but the same procedure fails to remove nucleic acid compounds from a culture which contains no volutin. The conclusion is therefore drawn that volutin itself is a nucleic acid derivative. The living cell, even if volutin is absent, contains zymase, catalase, and nuclease, the latter being able to liberate phosphoric acid from nucleic acids. The stimulation of fermentation by volutin is therefore probably due to the steady production of small quantities of phosphoric acid from it.

J. C. W.

The Plasmotype-Volumetric Method and its Applicability to the Measurement of the Osmotic Value of Living Plant Cells. KARL HÖFLER (*Ber. Deut. bot. Ges.*, 1917, 35, 706—726).—In the original experiments of de Vries, a comparison was made between the concentrations of the solutions of different substances which were just capable of producing perceptible plasmolysis in the immersed plant cells. When more concentrated external solutions are employed, plasmolysis takes place until the issuing water has reduced the volume of the cell sap to such an extent that the internal and external solutions are isotonic. By the use of suitable plant cells, it is possible to measure the volume of the protoplast when equilibrium has been reached by means of a measuring microscope, and from the relation between this volume and the volume of the cell, the osmotic concentration of the original cell sap may be calculated. The results obtained in a series of experiments in which the concentration of the external (sucrose) solution was varied show a close agreement. It seems possible that the method may be applied in the investigation of the deviations of the osmotic concentration of cells from the average or normal values.

H. M. D.

The Physiologically Active Constituents of certain Philippine Medicinal Plants. II. HARVEY C. BRILL and ALBERT H. WELLS (*Philippine J. Sci.*, 1917, 12, [A], 167—198. Compare A., 1907, ii, 500).—A continuation of the examination of medicinal plants occurring in the Philippine Islands. A summary of previous knowledge and of native applications of the plants is given in each case.

Lophopetalum toxicum, Loher (N.O., *Celastraceae*), is a tree from the bark of which the natives obtain a juice with which to poison their weapons, care being taken by them not to leave the extract in contact with sour substances. A yield of 0.8% of a very toxic saponin, crystallising in clusters of needles, m. p. 183°, was obtained from the fresh bast fibre.

The bark of *Erythrophloeum densiflorum*, Merrill (*Leguminosae*).

contains tannins but no alkaloids, the substance erythrophleine found in *E. guineense* being absent from this species.

Quisqualis indica, Linn. (*Combretaceae*), gives fruits with yellow kernels which have been a popular anthelmintic and laxative in the East for some centuries. The seeds contain a yellow oil, possessing purgative but not anthelmintic properties, a sugar, 3.87% of potassium sulphate, and a gum which shows many alkaloidal reactions.

Tylophora brevipes, F.-Vill. (*Asclepidaceae*), is valued by the Filipinos as an emetic and expectorant, a decoction of the root being used. The plant is closely related to *T. asthmatica*, well known in India for its resemblance in properties to ipecacuanha and it contains the same alkaloid, tylophorine (Hooper, A., 1891 1267).

Toddalia asiatica, Kurz (*Rutaceae*), has been widely known to centuries on account of the febrifugal and anti-diarrhoeal properties of its roots, being mentioned in old pharmacopœias as "*Radix indica lopeziana*," or *tinct. toddalia*, especially in India. Its active principle is berberine.

Lunasia amara, Blanco (*Rutaceae*), the native name for which signifies "bitterness itself," provides a close-grained wood which is so hard that the Negritos often use it for the tips of their arrows, but not to poison the weapons, as is wrongly supposed. The juice of the seeds is used against the bite of poisonous animals, and the bark and seeds are held to be useful in gastralgia. The bark and leaves contain about 0.6% of intensely bitter alkaloidal substances of moderate physiological activity, wholly or chiefly consisting of lunasine, already reported by Boorsma. Prior to Boorsma's work in 1900, it appears that all accounts of *Lunasia* were founded on specimens sent to European museums, which were really *Lophopetalum toxicum*.

Rourea erecta, Merrill (*Connaraceae*), is a vine, the roots and berries of which are used by native quack doctors for a variety of ailments. The berries, even old, dry specimens, contain an active principle which is very toxic to carnivora but not to herbivora.

Hymenodictyon excelsum (*Rubiaceae*) of the Philippines contains no alkaloid, but differs from Indian varieties in that the active febrifuge is not æsculin, but β -methylæsculetin (compare Gibson and Simonsen, this vol., i, 151). The product isolated had m. p. 203°, and gave an *acetyl* compound, rhombic prisms and plates, m. p. 177°, and agreed with Schmidt's compound from *Gelsemium sempervivens* (A., 1899, i, 72). J. C. W.

General and Physical Chemistry.

The Optics of Disperse Systems. I. I. LIFSCHITZ (*Kolloid Zeitsch.*, 1918, 22, 53—57).—A general discussion of the optical properties of disperse systems, including the absorptive power, the refractivity, and the rotatory power of optically active colloids.

H. M. D.

The Relation between the Degree of Supersaturation, the Refractive Index and the Temperature of Sugar Solutions.

E. V. MILLER and F. P. WORLEY (*J. Soc. Chem. Ind.*, 1918, 37, 98—103r).—Measurements have been made of the refractive index of supersaturated solutions of sucrose with the object of determining the influence of temperature and concentration on the refractive index between 30° and 75° and between 72% and 81% of sucrose, which range of concentration is of technical importance. The results obtained show that the refractive index, in its dependence on the temperature t and the percentage concentration p , can be satisfactorily represented by the equation $r = 1.28534 - 0.0001241t + (0.00263 - 0.000001267t)p$. This equation may be written in an alternative form, in which r is represented as a function of the temperature and the degree of supersaturation s , the relation between p and s being given by $p = 100(S + s)/100 + S + s$, in which S represents the number of parts of sucrose per 100 of water in the saturated solution. A table is given showing the values of the refractive indices of solutions for $s = 0$ to $s = 110$, and for temperatures ranging from 43.3° to 76.6°.

H. M. D.

The Arc Spectrum of Europium and a New Element, Eurosamarium, between Europium and Samarium.

JOSEF MARIA EDER (*Sitzungsber. K.K. Akad. Wiss. Wien*, 1917, IIA, 126, 473—531; from *Chem. Zentr.*, 1918, i, 70—71).—Europium imparts a fine red colour to the electric arc, and its characteristic groups of lines are very bright and easily distinguished. The author has examined the photograph of the spectrum of one of Urbain's preparations, which proved to be remarkably pure, and has also tested two samples supplied by Auer, the one being a europium fraction related to gadolinium and the other a specimen akin to samarium. In these, he has measured 1171 europium lines between 7370 and 2373. The lines which were obtained with the material quite free from samarium included some which are ascribed to a new element, *eurosamarium*, and these are tabulated in the original.

J. C. W.

Atomic Weights of the Elements in Nebulæ. J. W. NICHOLSON (*Month. Not. Roy. Astr. Soc.*, 1918, 78, 349—362).—

A theoretical paper in which equations are derived for the periods

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of vibration of atoms with a single ring of electrons. These equations, in combination with the wave-lengths of the principal lines in the spectrum of nebulium, give for m/M the value 0.000415, in which m is the mass of an electron and M the mass of the atom. Assuming that for hydrogen $m/H = 0.000545$, the atomic weight of nebulium is found to be 1.31, with a possible error of one unit in the second decimal place.

H. M. D.

The Shifting of Radioactive Equilibria under the Influence of Fluorescein. H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 768—772. Compare A., 1917, i, 241).—The antagonism between potassium and uranium in their influence on the pulsation of the frog's heart is found to be appreciably affected by the addition of fluorescein in the sense that a larger quantity of potassium is required to antagonise a given quantity of uranium if fluorescein is added to the solution. The displacement produced by fluorescein is in the same direction as that which, according to observations on summer and winter frogs, is produced by a rise of temperature.

H. M. D.

Radioactivity of Waters of the Mountainous Region of Northern Luzon (Philippines). GEORGE W. HEISE (*Philippine J. Sci.*, 1917, 12, [A], 293—307).—In continuation of previous work (Wright and Heise, A., 1917, ii, 560), the author has examined the waters of a number of springs and wells in northern Luzon. The region shows evidence of recent vulcanism. The data are not yet numerous enough to warrant general conclusions, but they do not confirm the usual observation that radioactivity is most common among waters from volcanic regions, or at least among thermal springs. Of the numerous salt springs and hot springs examined, none showed high radioactivity. The most active waters were rich in calcium and magnesium, indicating an origin in calcareous material. High activity was found only in waters from a small district (Ifugao), and was probably due to the presence of local deposits of radioactive material.

J. H. L.

Constancy in the Radioactivity of certain Philippine Waters. GEORGE W. HEISE (*Philippine J. Sci.*, 1917, 12, [A], 309—311).—Measurements of the radioactivity of the water of a Philippine spring at different periods of the year showed no appreciable changes, in spite of great variations in the rate of flow of the spring. The composition of the water is substantially the same as in 1890.

J. H. L.

Extrapolation of Conductivity Data to Zero Concentration. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1918, 40, 622—623).—Polemical, in which the author claims priority over Washburn (this vol., ii, 55) in the method employed by the latter for the calculation of the zero concentration values of conductivity data. [See T., 1912, 101, 1279, 1291.]

J. F. S.

Electrolytic Dissociation in Solvents with Low Dielectric Constants. V. A. PLOTNIKOV (*Reprint*).—From theoretical considerations and the results of conductivity measurements on various solutions, the following conclusions are drawn. Solvents with low dielectric constants are capable of forming solutions showing high electrical conductivity. The conductivity of a solution depends to as great an extent on the solute as on the solvent; these two must be in peculiar electrochemical correspondence in order that they may yield a conducting solution. The phenomenon of electrical conductivity in a solution cannot be explained by any definite property of the solvent conditioning its dissociating capacity; electrochemical investigation of a solution has to deal with a conducting "couple." Electrochemical correspondence is explained as due to the resonance of the movement of the solvent molecules with the ionic vibrations of the electrolyte. T. H. P.

Electrochemical Potential and the Periodic Law. J. C. THOMLINSON (*Chem. News*, 1918, 117, 176).—The relation between electrochemical potential and the position of the elements in the periodic system is demonstrated by means of a curve. In this curve, starting with the most electropositive element, caesium, the elements follow the order caesium to lithium (as in group I), barium to magnesium (as in group II), aluminium, chromium, manganese, zinc, cadmium, iron, cobalt, nickel, hydrogen. The non-metals then continue the curve, and these, after silicon, carbon, and boron, all occupy positions in the upper right-hand corner of the periodic table. J. F. S.

The Passivity of Chromium. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 812—823).—The values recorded in the literature for the potential of the chromium electrode are very divergent, and this is supposed to be connected with the tendency of the metal to assume the passive condition. Electrodes were prepared from chromium obtained by Goldschmidt's method, by the electrolysis of solutions containing a mixture of chromic sulphate and chromic acid, and by the electrolysis of solutions of chromic chloride. These were brought into contact with a 0.3 molar solution of chromous sulphate and combined with a normal calomel electrode.

The results obtained indicate that the potential of chromium in contact with chromous sulphate solution is about -0.75 volt, or -0.47 volt when referred to the hydrogen electrode. This active potential value is only attained when hydrogen is present in the metal in sufficient quantity. The hydrogen appears to act as a catalyst in promoting the establishment of the electrode equilibrium. H. M. D.

Potential Measurements on the Copper-Nickel Series of Alloys and some observations on Brasses. NEWELL T. GORDON and DONALD P. SMITH (*J. Physical Chem.*, 1918, 22, 194—215).—A study of the factors affecting the potential differ-

ence between a binary (solid) alloy and an electrolyte containing the corresponding ions (see A., 1916, ii, 214). With copper-nickel alloys, no treatment employed was sufficient to ensure reproducibility or constancy in the "steady" potential finally attained, but copper-nickel alloys are shown to be very regular in electrochemical conduct, and the potential values are reproducible and constant for many hours.

Six ingots of copper-nickel alloys, containing 6.8, 10.9, 65.3, 74.3, 83.4, and 94.7% of Cu were carefully prepared, and a small test-piece $2 \times 2 \times 2\frac{1}{2}$ mm. cut from each, the end surface of each bar forming a portion of a horizontal plane passing through the middle of the ingot, and this was the part exposed afterwards to the electrolyte. Each piece was annealed in an atmosphere of nitrogen, the first two at 218° and the others at 600° . The electrolytes employed were all *N/1*-solutions of copper and nickel sulphates combined, and some contained in addition *N/1*-sodium sulphate. All potentials were measured at 25° against a normal calomel electrode by means of a potentiometer and a galvanometer. For some time after immersion the potential changes rapidly, but after some hours a steady value is reached, which afterwards remains constant within 3 millivolts during the period of observation. It is found that carefully annealed specimens give the most constant results, and although there are no regular differences between the steady potentials of surfaces annealed and treated with emery, yet the latter exhibit greater accidental variations. Polished surfaces have a greater tendency to give ions to the solution. With alloys from a given ingot, and also with ingots of a similar composition, it was found that the steady potential is definitely determined by the composition of the electrolyte. The potential differences exhibited are expressible by a relation which is linear both with respect to alloy composition and to the logarithm of electrolyte composition.

It is shown that copper sulphate concentration may be employed without any sacrifice of accuracy in the representation of the empirical results in place of the cupric ion concentration required by Nernst's thermodynamic theory, provided the constants of the equation are altered.

B. N.

The Lead Electrode. II. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 611—619).—Since the publication of the previous paper (A., 1916, ii, 287), the question of the possible allotropy of lead has arisen. The present work was undertaken to furnish an answer to this question. The *E.M.F.* of cells of the type $\text{Pb} | 0.1M\text{KCl sat.} | \text{PbCl}_2 || 0.1M\text{KCl}, \text{Hg}_2\text{Cl}_2 | \text{Hg}$ has been measured at 25° , using lead electrodes from various sources as treated in different ways. It is shown that the value of the *E.M.F.* obtained with different specimens of lead cast into sticks with electrolytically deposited lead, and with lead amalgams, was the same in all cases. The normal electrode potential of lead as calculated from the results to be 0.4121 volt referred to the

v-calomel electrode and 0.1293 volt against the *N*-hydrogen electrode. The values of the *E.M.F.* of cells containing electrodes which had been immersed for varying periods of time in Heller's solution (400 grams lead nitrate, 1000 c.c. water, and 100 c.c. nitric acid [*D* 1.16]) were found to be about 8 millivolts higher than the values obtained with cells containing electrodes which had not been subjected to this treatment. The temperature coefficient of the cell was found to be 0.00022. The heat of the reaction $\text{Pb} + \text{Hg}_2\text{Cl}_2 = \text{PbCl}_2 + 2\text{Hg}$ was calculated, and found to be 21,840 cal., and the heat of formation 84,440 cal. The heat of reaction U_0 and the maximum work A_{234} were calculated by means of the Nernst-Lindemann equation, and the value of the *E.M.F.* at 234°A computed. The values $U_0 = 24,035$ cal., $A_{234} = 24,041$ cal., were obtained, and the value of the *E.M.F.* was in close agreement with the experimental value.

J. F. S.

The Quantum Theory of Paramagnetism. FRITZ REICHE (*Ann. Physik*, 1917, [iv], 54, 401—436).—A mathematical paper in which the quantum hypothesis is applied in the development of a theory of paramagnetism. The formula derived for the relation between the magnetic susceptibility and the temperature is tested by reference to the available data for ferrous sulphate and manganous sulphate, and found to be quite satisfactory. H. M. D.

Investigations on the Thermal Conductivity of Gases. I. and II. SOPHUS WEBER (*Ann. Physik*, 1917, [iv], 54, 325—356, 437—462).—The sources of error involved in the determination of the thermal conductivity of gases by Schleiermacher's method are subjected to a critical analysis, and a modified form of apparatus is described in which the errors due to convection are greatly reduced. With this improved form of apparatus, measurements have been made of the thermal conductivity of a number of gases.

The following values are recorded: hydrogen, 4.165×10^{-4} ; neon, 1.089×10^{-4} ; helium, 3.438×10^{-4} ; argon, 3.850×10^{-5} ; nitrogen, 5.660×10^{-5} ; oxygen, 5.768×10^{-5} ; methane, 7.200×10^{-5} ; carbon dioxide, 3.393×10^{-5} ; nitrous oxide, 3.530×10^{-5} . The results are discussed in reference to certain aspects of the theory of the conductivity of gases.

H. M. D.

The Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 750—767).—A theoretical paper in which the author discusses the influence of temperature and volume on the constants a and b of the van der Waals's equation. It has been suggested by van der Waals that a varies with the volume if the temperature is lower than the critical temperature, but the author's arguments lead to the conclusion that a depends only on the temperature, whether this is above or below the critical temperature. On the other hand, b appears to be a function of both temperature and volume.

H. M. D.

The Saturated Vapour Pressures of Triatomic Liquids. E. ARIÈS (*Compt. rend.*, 1918, 166, 668—672. Compare this vol., ii, 61).—Using the known physical constants for carbon dioxide, the author deduces the formula $\Pi = \tau^{1/3} Z/x$, where $x = [1 + (1 - \tau)^{0.88 - \tau})/0.40(\tau^2 + 1)]^{1/2}$ for the saturated vapour pressures of triatomic liquids. The observed results are in fairly close agreement with those calculated by this formula in the cases of sulphur dioxide and nitrous oxide, but this is not true for hydrogen sulphide and water. W. G.

The Adsorption of Sodium Gold Chloride by Charcoal. The Estimation of Gold in Sea-water. HELLMUTH KOCH (*Kolloid Zeitsch.*, 1918, 22, 1—22).—The adsorption of gold from very dilute solutions of gold chloride in 3% sodium chloride by various forms of carbon has been examined with a view to the application of the adsorption process in the estimation of gold in sea-water. Measurements of the rate of the adsorption show that this takes place fairly rapidly, but the attainment of a condition of equilibrium is prevented by the fact that the adsorbed gold salt is slowly reduced, and in consequence of this there is a continuous fall in the concentration of the gold in the aqueous solution. The concentration time curve consists accordingly of two branches of very different slopes, the intersection of which affords a sufficiently accurate measure of the adsorption effect.

The results obtained for solutions of varying concentration are satisfactorily represented by means of the ordinary adsorption equation. Finely divided wood charcoal was found to be the most satisfactory adsorbent, and this material was used in experiments on sea-water, three samples of which gave results indicating the presence of 2.5 to 4 mg. of gold per cubic metre. These values for the quantity of gold in sea-water are in agreement with the results obtained by some earlier observers, although much larger values have been recorded. The literature of the subject is discussed in detail. [Compare *J. Soc. Chem. Ind.*, June.] H. M. D.

Influence of Neutral Salts on the Dissociation Constants of Indicators. I. M. KOLTHOFF (*Chem. Weekblad*, 1918, 15, 394—400).—The dissociation constants of phenol, aniline, and colorimetric indicators are increased by addition of neutral salts. This fact explains the development of the alkaline tint on addition of a neutral salt to an acid indicator, and the corresponding development of the acid tint of an alkaline indicator. The effect is very marked in the case of azolitmin. A. J. W.

[Diffusion of Gases through Indiarubber.] SIR JAMES DEWAR (*Proc. Roy. Inst.*, 1918, 21, 813—826).—An appendix to a lecture on "Problems of Hydrogen and the Rare Gases" (compare *ibid.*, 543). An account is given of apparatus which has been used by the author in the investigation of the diffusion of gases through thin rubber membranes at varying pressures and temperatures.

With a membrane about 0.01 mm. thick, the rates observed for different gases, at atmospheric pressure and 15°, in c.c. per day per cm.² were: air, 2.0; nitrogen, 1.38; carbon monoxide, 1.88; helium, 3.5; argon, 2.56; oxygen, 4.0; hydrogen, 11.2; carbon dioxide, 28.0. The order in which the gases are arranged according to their diffusibility does not appear to be directly related to any chemical or physical property of the gases concerned.

The rate of diffusion increases rapidly with rise of temperature, and when the logarithm of the rate is plotted against the temperature, straight line graphs are obtained. These lines all show a distinct break at 0°, which suggests that water is in some way involved. In the case of carbon dioxide, a much more pronounced break is found at -37°.

The composition of the gaseous mixture resulting from the diffusion of air through rubber has been examined by ordinary chemical analysis and also by the spectroscopic investigation of the residue obtained after subjecting the mixture to the action of charcoal cooled in liquid air. By this means, it has been found that the hydrogen and helium in air diffuse at nearly the same rate, whilst the rates of diffusion of helium and neon are as 9 to 1.

Observations were also made on the diffusion of gases through rubber membranes immersed in different liquids, such as water, salt solutions, ethyl alcohol, and glycerol.

H. M. D.

Diffusion in Anisotropic Liquids. THE SVEDBERG (*Kolloid Zeitsch.*, 1918, **22**, 68—71).—In view of the necessity of maintaining a constant temperature in the diffusion experiments, the author has made use of an equimolecular mixture of *p*-azoxyanisole and *p*-azoxyphenetole. This mixture, which melts at 95° and becomes isotropic at 150°, is convenient for the observations in that the diffusion measurements may be made at 100°. The rate of diffusion of *m*-nitrophenol in the anisotropic liquid was measured (a) in the absence of an external magnetic field, (b) in a longitudinal magnetic field, and (c) in a transverse magnetic field. The results obtained show that the rate of diffusion is increased by the application of the longitudinal field and diminished when the direction of the field is transverse to that in which diffusion takes place.

H. M. D.

Kinetic Theory of Osmotic Pressure and of Raoult's Law. II. G. JÄGER (*Ann. Physik*, 1917, [iv], **54**, 463—480. Compare A., 1913, ii, 762).—A theoretical paper devoted to the consideration of the kinetic interpretation of osmotic pressure and of Raoult's vapour pressure law.

H. M. D.

Manifestation of Osmotic Pressure with Membranes of Chemically Inert Materials. S. L. BIGELOW and C. S. ROBINSON (*J. Physical Chem.*, 1918, **22**, 153—183).—A method and apparatus have been devised for the study of osmotic phenomena with membranes of powdered materials, such as silica,

amorphous carbon, graphite, metallic copper, gold, and silver. The membranes were prepared by alternately pressing the purified material under a high pressure and clogging the pores by sucking a fine material in suspension through the membranes. Thus, in the case of pure silica, a pressure of 350 kilos. per cm. was used, and the largest pores in two membranes were reduced to 1.4823 and 0.3488 microns respectively. Amorphous carbon was prepared by ignition of a pure sucrose, compressed, and clogged as above, but the pore diameters in this, and in flaky graphite washed with acid and similarly treated, had to be considerably reduced to produce osmosis. Reduced copper and silver powders had to be pressed for several days at 350—450 kilos. per cm. to reduce the diameters, and the results show generally that the magnitude of osmotic effects increases with a decrease in the diameters of the pores of the membrane. It appears to be fairly obvious that the various examples of osmosis are not due to one but to a variety of causes, and according to the various theories osmosis may take place (1) through capillary spaces in the membrane, (2) by solution of the solvent in the membrane, (3) by the formation of a labile chemical compound between the membrane and the solvent. The present work has demonstrated that osmotic pressure can be produced through the agency of capillary forces alone, without the aid of solution processes or chemical reactions.

B. N.

Theory of Solutions. Solubility Studies in Ternary Mixtures of Liquids. JOHN HOLMES (T., 1918, 113, 263—275, Compare T., 1913, 103, 2147).—In the further investigation of the theory that the miscibility of liquids is determined by the possibility of the close-packing of the different kinds of molecules, and is therefore dependent on the relative molecular radii, the author has examined a number of three-component systems.

The theory indicates that these liquids should be miscible in all proportions if the molecular radii are equal. If the molecules are of different sizes, the dimensions of the interspaces will decrease as the ratios between the several radii increase until a point is reached at which close packing is a maximum. In the case of an equimolecular mixture this occurs when the radii are as 1.682:1.466:1. If the respective ratios are greater than these limiting values which correspond with the border line between complete and partial miscibility, separate layers are formed.

So long as the radial ratio of the two smaller molecules is not greater than 1.618 and the corresponding ratio for the extreme molecules exceeds 1.682, but is less than $(1.618)^2$, the mixture should separate into two layers only. If the ratios are greater than these values, three separate layers are to be expected.

In the expectation that the higher paraffin hydrocarbons would afford liquids for which the molecular radii compared with water are greater than $(1.618)^2$, the author has examined the miscibility of various binary mixtures of petroleum and water with a third

substance. Three-layer systems were obtained with aniline, phenol, nicotine, and nitrobenzene, and the behaviour of these mixtures is described.

Three liquid layers were also found in the case of mixtures of petroleum, glycerol, and nitrobenzene. H. M. D.

Condition of Substances in Solution in Absolute Sulphuric Acid. VIII. G. ODDO [with A. CASALINO]. (*Gazzetta*, 1918, 48, i, 17—44).—The author uses the results of his previous measurements, some of which have now been repeated and confirmed, to refute the criticisms of Hantzsch (*ibid.*, 1911, 41, i, 645). T. H. P.

Flocculation. SPENCER UMFREVILLE PICKERING (*Proc. Roy. Soc.*, 1918, [A], 94, 315—325).—Experiments have been made to determine the effect of freezing on the sedimentation of certain voluminous precipitates, such as basic copper sulphate, cupric hydroxide, ferric hydroxide, and aluminium hydroxide, and also on clay and kaolin. In all cases, sedimentation takes place more rapidly after freezing, and the volume of the sediment from the liquids which have been frozen is considerably smaller than that from liquids which have not been subjected to this treatment. The shrinkage observed varies from 40 to 90%, and is probably due to dehydration.

The flocculation of suspensions of kaolin on the addition of various substances has been examined, with results which show that the process is accompanied by a considerable increase in the volume of the particles. The increase in the volume of the sediment when acids or salts are used as the flocculating agents is closely related to the quantity of kaolin remaining in suspension, the latter becoming nil when the former reaches a maximum. When the added substance produces no flocculation, there is no increase in the volume of the sediment. In explanation of these relations, it is suggested that the kaolin combines with the flocculant. H. M. D.

Jellies Formed by Dyes. R. HALLER (*Kolloid Zeitsch.*, 1918, 22, 49—57).—It has been observed that hot concentrated solutions of substantive dyes produce jellies when the solutions are allowed to cool. Experiments made with benzopurpurin 4 B and chrysophenin B show that the formation of these jellies is dependent on the presence of small quantities of electrolytes in the dyes. If a 1% solution of either of the dyes is subjected to dialysis, the electrolytes are removed and the contents of the dialyser separate into two parts, one of which is liquid and the other of gelatinous consistency. The latter does not dissolve even when heated to 100°, and it seems probable that the colloidal dye has been rendered insoluble by the removal of the electrolytes. If the dialysed substance is dried and powdered, the product is markedly different from the original dye in its small solubility

in water. The purified substance dissolves quite readily, however, if sodium chloride is added to the water.

The structure of the benzopurpurin 4 B jellies has been examined and found to be very similar to that of the soap jellies described by Zsigmondy and Bachmann (A., 1912, ii, 1149). [See, further, *J. Soc. Chem. Ind.*, June.] H. M. D.

The Quaternary System, $\text{AgNO}_3\text{-NH}_4\text{-NO}_3\text{-Ba(NO}_3)_2$ -Water at 30°. (Miss) W. C. DE BAAT (*Chem. Weekblad*, 1918, 15, 463—468).—An application of Schreinemakers's graphic method to aqueous solutions of the nitrates of silver, ammonium, and barium at 30°. A. J. W.

A Method of Obtaining General Reaction-Velocity Curves for Complete Homogeneous Gas Reactions at Constant Pressure. GEORGE W. TODD (*Phil. Mag.*, 1918, [vi], 35, 435—444. Compare this vol., ii, 102).—The method previously described for the derivation of curves representing the progress of homogeneous reactions at constant volume has been extended to the case of binary gas reactions taking place at constant pressure.

For a bimolecular reaction of the type $A+B\rightarrow$, in which a gram mols. of A react with b gram mols. of B , v is the total volume of reactants and resultants, and x the number of gram mols. transformed in time t , the equation for the velocity of the reaction when B is in excess may be written in the form $dX/dt = k \cdot a/v_0 \cdot (1-X)(p-X)$, where $X=x/a$, $p=b/a$, and v_0 is the original value of v . Since the right-hand side of this equation does not involve the constant, which, in a particular case, is determined by the ratio between the numbers of mols. of reactants and resultants, it follows that the general curves previously given will be applicable to the case of bimolecular reactions at constant pressure as well as at constant volume.

Termolecular reactions of the type $2A+B\rightarrow$ with A and B in excess are also considered, and general equations devised for these. The curves which are plotted from these equations show the change of X with t for different values of $p=b/a$, and two sets of diagrams are given corresponding with the case where the volume of the resultants is $2/3$ and $1/3$ respectively of the volume of the reactants. This volume change is expressed in the general equation for the velocity by means of a quantity a , in terms of which, if B is present in excess, $v=v_0\{3a(1+aX)+(b-a)\}/3a+(b-a)$, and if A is present in excess, $v=v_0\{3b(1+aX)+2(a-b)\}/3b+2(a-b)$. H. M. D.

Periodic System of the Elements. P. V. WELLS (*J. Washington Acad. Sci.*, 1918, 8, 232—234).—The author has redrawn the spiral periodic table of Stoney and others as revised by Harkins and Hall, and has given it a period of 8 instead of 16. The distance from the centre of the spiral to an

element represents the atomic weight, and the elements are arranged in angular order of atomic number, each group being placed radially with the sub-groups slightly displaced. The metals of positive valence are sharply separated from the non-metals of negative valence. The proposed arrangement is much simpler than the double helix and has all its advantages; it overcomes the artificiality of the 16-period table and brings the main groups and sub-groups together. The new table is particularly adapted to illustrating the electron theory. The possibility of two forms of neon is indicated.

A. B. S.

Characteristic Frequency and Atomic Number. H. STANLEY ALLEN (*Proc. Roy. Soc.*, 1917, [A], **94**, 100—111. Compare this vol., ii, 14, 15, 163).—The relation between the atomic number and the characteristic frequency of an element is considered with reference to the theory of probability, and it is shown that the chance of the relation being accidental is very small.

According to Rydberg, there are two unknown elements between hydrogen and lithium, and the atomic number of lithium should be taken as 5 instead of 3, which is the value assigned by Moseley. The relation $N\nu = \nu\nu_A$ fits the results of observation more closely, however, when Moseley's numbers are used for N . With regard to the physical significance of the relation, it is supposed that the energy of the nucleus is an integral multiple of a certain quantity of energy characteristic of that condition of the atomic system which corresponds with the limiting frequency.

The similar relation connecting the atomic number and the electronic frequency is supposed to indicate that in the limiting conditions which are associated with the maximum of the photo-electric effect, the ionisation potential, and the thermionic potential we are dealing with a minimum value of the energy of the atomic system.

H. M. D.

Molecular Frequency and Molecular Number. II. The Frequency of the Longer Residual Rays. H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], **35**, 404—409. Compare this vol., ii, 14, 163).—According to the results previously communicated, it would seem that the product of atomic number and atomic frequency in the case of an element, or of molecular number and molecular frequency in the case of a compound, is an integral multiple of a fundamental frequency which is approximately equal to 21×10^{12} sec.⁻¹ In order to obtain the frequency of vibration of the atoms in compounds, recourse may be had to the residual rays which are obtained by repeated reflections from the surfaces of solids, and have been investigated by Rubens (compare A., 1910, ii, 172; 1913, ii, 648; 1914, ii, 236). By reference to the available data for the wave-lengths of the residual rays for various inorganic compounds, further evidence is obtained in support of the above relation between the molecular number and the molecular frequency.

The results obtained in this and the preceding papers suggest that the forces binding the atoms in the molecule are similar in character to those which bind the molecules of a solid. To account for the integral relations, it must be assumed that there is something of a discrete character in the nature of these forces, and the suggestion is made that the linkings between the atoms are constituted by Faraday tubes of force, which would then be regarded as physical entities.

H. M. D.

Device for Preventing Back-flow in Water Pumps. MESTREZAT (*Ann. Chim. anal.*, 1918, **23**, 84—85).—An ordinary bicycle valve suitably fitted in the pipe connecting the pump with the vessel from which the air is to be exhausted prevents water passing into the latter.

W. P. S.

Modification of the Soxhlet Extractor. J. W. WEIR (*J. Lab. and Clin. Med.*, *St. Louis*, 1917, **3**, 204; from *Physiol. Abstr.*, 1918, **3**, 4).—A modification for use in the extraction of liquids is described and figured in the original.

W. G.

New and Simple Ultra-filters. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1918, **22**, 72—76).—Ultra-filters of simple construction for the filtration of colloidal solutions are described. It has been found that an efficient apparatus may be obtained by the use of either an ordinary or a Büchner funnel and filter paper which has been treated in situ with a 2% collodion solution. The best results were obtained, however, by the use of a Schleicher and Schüll Filtrierhut M577 treated in the same way with the colloidal solution. The results obtained by subjecting a number of colloidal solutions of different kinds to ultra-filtration in this apparatus are described.

H. M. D.

Inorganic Chemistry.

Recovery of Iodine from Dilute Residues. HERBERT F. STEPHENSON (*Analyst*, 1918, **43**, 165—166).—The iodine is precipitated as mercuric iodide by treating the neutral or slightly acid liquid with mercuric chloride; when a suitable quantity of the iodide has been collected, it is treated at about 45° with a mixture of nitric and hydrochloric acids (1:5), then cooled, and the liberated iodine collected. Four parts of the moist iodine are now added in small quantities to a mixture of 1 part of iron filings and 10 parts of water; the mixture is boiled subsequently, treated with a slight excess of potassium hydroxide, the precipitated ferric hydroxide is separated, and the potassium iodide recovered by evaporating the solution. [See, further, *J. Soc. Chem. Ind.*, June]

W. P. S.

A Third Kind of Sulphur Molecule. V. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 824—830. Compare A., 1915, ii, 254).—Equilibrium between the two forms of sulphur, S_8 and S_2 , is attained less rapidly in toluene than in sulphur chloride. At 140° , six hours are required in the case of toluene, whereas equilibrium is reached in a few minutes in sulphur chloride solution.

Solutions of sulphur in toluene, in which equilibrium between S_8 and S_2 had been established by heating at 140° , 150° , and 160° , were cooled to 0° and stirred for an hour in contact with rhombic sulphur; the sulphur content of the resulting solution was then determined, and from the results the proportions of S_8 and S_2 in the solutions examined are derived. The proportion of S_2 increases with the temperature and also slightly with the concentration. Under similar conditions, the proportion of S_2 is considerably smaller in toluene than in sulphur chloride, but is approximately the same when toluene and carbon disulphide are used as solvents.

H. M. D.

Selenic Acid and Iron. Reduction of Selenic Acid by Nascent Hydrogen and Hydrogen Sulphide. Preparation of Ferrous Selenate and Double Selenates of the Iron Group.

A. E. H. TURTON (*Proc. Roy. Soc.*, 1918, [A], **94**, 352—361).—In an attempt to prepare ferrous selenate by the action of metallic iron on a solution of selenic acid, it was found that the iron becomes covered with a film of selenium which greatly retards the reaction and renders this method practically useless. No hydrogen is evolved, and the formation of the selenium would appear to be due to the reducing action of nascent hydrogen on the selenic acid, $3H + H_2SeO_4 = Se + 4H_2O$. The net result of such slow action as occurs may therefore be represented by the equation $3Fe + 4H_2SeO_4 = 3FeSeO_4 + Se + 4H_2O$. When the iron is replaced by zinc, hydrogen is given off, and very little reduction of selenic acid occurs. In the case of magnesium, hydrogen is also evolved, but reduction takes place to a considerable extent.

The reaction between ferrous carbonate (in the form of malachite) and selenic acid also occurs very slowly, and for this reason cannot be used for the preparation of ferrous selenate. Solutions of this substance were readily obtained, however, by the action of ferrous sulphide on a concentrated solution of selenic acid. The hydrogen sulphide liberated in the primary reaction reduces the selenic acid to some extent in accordance with the equation $3H_2S + H_2SeO_4 = Se + 3S + 4H_2O$, but this does not interfere with the application of the method. If the filtered solution is allowed to crystallise, monoclinic crystals of $FeSeO_4 \cdot 7H_2O$ isomorphous with $FeSO_4 \cdot 7H_2O$ are obtained. The crystals of the selenate are much less stable than those of ferrous sulphate, and become opaque with such rapidity that it has not been possible to make any accurate goniometric observations with them.

The double selenates of the type $M_2SeO_4 \cdot FeSeO_4 \cdot 6H_2O$ are

readily obtained in the case of rubidium, caesium, and ammonium. The corresponding potassium double selenate crystallises out if the temperature is not much higher than 0° . At the ordinary temperature, very small, monoclinic crystals of the dihydrated salt separate out.

H. M. D.

Telluric Acid and its Alkali Salts in their Behaviour as Semi-colloids. ARTHUR ROSENHEIM and GERHART JANDER (*Kolloid Zeitsch.*, 1918, **22**, 23—44).—The investigation of telluric acid and its alkali salts has shown that these readily undergo polymerisation, with the formation of substances of semi-colloidal or colloidal character, according to the degree of polymerisation.

Measurements of the hydrogen ion concentration of 1*N*-telluric acid solution gave $[H^+] = 4 \times 10^{-5}$ gram ion per litre. On the assumption that the acid ionises in accordance with the equation $H_6TeO_6 = H^+ + H_5TeO_6'$, this gives $K = 1.6 \times 10^{-4}$ for the ionisation constant. According to this result, telluric acid is a very weak acid, approximating very closely to boric acid and hydrocyanic acid. This is in agreement with the very small value of the molecular conductivity, which increases from 0.1902 for $v=4$ to 0.6913 for $v=1024$ litres per gram molecule.

Freezing-point and boiling-point measurements for telluric acid solutions were also made, and these observations are in general agreement with the evidence afforded by the electrical measurements. Irregularities in the boiling points were found which are attributed to the formation of modifications of telluric acid of colloidal character. That the constitution of the aqueous solutions changes with rise of temperature is shown by the abnormally large value of the temperature coefficient of the molecular conductivity. The facts suggest that the more complex modification formed as the temperature rises is more strongly ionised than the modification which is represented by the crystalline acid. The so-called *allotelluric acid* described by Mylius (A., 1901, ii, 550) represents such a polymerised modification of greater conductivity. When aqueous solutions of *allotelluric acid* are kept at 25° , the conductivity falls, and ultimately reaches the value which is characteristic of the crystallised acid. The depolymerisation is also shown in other properties of the solution, but the milky appearance indicates that small quantities of a colloidal, insoluble modification are present. In view of this behaviour, it would seem that *allotelluric acid* is not a homogeneous modification, but consists of a mixture of polymerised forms differing considerably in complexity.

The investigation of the sodium, lithium, and potassium salts has shown that these behave in many ways like the free acid. These salts have no definite solubility in water; the quantity of water which the crystals contain varies according to the concentration of the solutions from which they are deposited, and the crystals undergo dehydration without any appreciable change in appearance. In these and other respects the salts resemble colloids. They not only absorb water, but experiments made with

lithium tellurate show that the basic salts which have been described are in all probability adsorption compounds formed by the adsorption of lithium hydroxide from the solution. In a similar way, experiments made with potassium tellurate indicate that the so-called acid salts are adsorption compounds containing variable proportions of adsorbed telluric acid. In view of these observations, the statements made with respect to the alkali tellurates in the older literature must be accepted with reserve.

In the course of this investigation, solutions containing telluric acid and potassium nitrate was found to deposit large crystals of the composition $2\text{KNO}_3 \cdot \text{H}_6\text{TeO}_6 \cdot 2\text{H}_2\text{O}$. This substance can be recrystallised from dilute solutions of potassium nitrate without decomposition. With silver nitrate, the acid forms the compound $\text{AgNO}_3 \cdot \text{H}_6\text{TeO}_6$.

Reference is made to the fact that telluric acid readily crystallises with other salts, for example, with phosphates, arsenates, iodates, and oxalates. The formation of these additive compounds is supposed to be connected with the weak acid nature of telluric acid.

H. M. D.

Recent Studies on Active Nitrogen. (Hon.) ROBERT JOHN STRUTT (T., 1918, 113, 200—209).—A lecture delivered before the Chemical Society on February 21st, 1918.

H. M. D.

Nitride Formation. E. B. MANTON (*J. Soc. Chem. Ind.*, 1918, 37, 105—109).—The available data for the influence of temperature on the specific heats of nitrogen, hydrogen, and ammonia lead to the conclusion that the equilibrium $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ will be displaced with rise of temperature in favour of the elementary gases, but that the proportion of ammonia will reach a minimum at a certain temperature and at higher temperatures will increase as the temperature rises. With the object of testing this result, which depends on an extrapolation of the formulae connecting the specific heats of the gases with the temperature, the author has investigated the formation of ammonia at high temperatures by rapidly cooling the hot gaseous mixtures.

In one of the methods employed, the mixture of nitrogen and hydrogen was injected into an oxy-hydrogen flame burning under water, the ammonia contained in the water at the end of the experiment being estimated colorimetrically or by direct titration. The proportion of the injected mixture of nitrogen and hydrogen was varied in different experiments, resulting in changes in the flame temperature which could be approximately estimated. From the quantities of ammonia actually found in the several experiments, the author calculates the amount which would have been formed if the gas mixture consisted entirely of nitrogen, hydrogen, and ammonia at atmospheric pressure. In this way, it has been found that the proportion of ammonia increases from 0.0027 vol. % at 1230° (abs.) to 1.23 vol. % at 2580° (abs.).

In other experiments, the flame was cooled by contact with a water-cooled quartz tube. Under these conditions, the cooling is

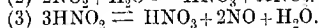
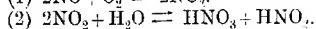
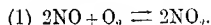
less rapid, and although these experiments show also that the equilibrium proportion of ammonia increases rapidly with the temperature, the quantities obtained were less than those in which the hot gaseous mixture was directly cooled by water.

The possibility of obtaining iron nitride by direct combination of nitrogen with the finely divided metal has also been examined. Although iron nitride begins to give off nitrogen at about 500° and decomposes rapidly at 600° , experiments in which finely divided iron was subjected to the action of nitrogen at 100 atmospheres between 500° and 700° showed no evidence of the formation of nitride. In view of this negative result, attempts were then made to determine the dissociation pressure of iron nitride. The nitride was slowly raised in temperature to 600° , and then allowed to cool slowly, the pressure being read off at various temperatures. Experiments were made for various initial nitrogen pressures, and although in all cases decomposition of the nitride took place at 600° , there was no evidence of recombination during the cooling process. In other words, equilibrium conditions are not realisable. The results obtained, however, suffice to show that iron nitride cannot be synthesised under the conditions obtaining in these experiments.

H. M. D.

The Production of Nitric Acid from Nitrogen Oxides.

GUY B. TAYLOR, JULIAN H. CAPPS, and A. S. COOLIDGE (*J. Ind. Eng. Chem.*, 1918, 10, 270–275).—If a mixture of nitric oxide with excess of air from an oxidising plant is cooled and allowed sufficient time to oxidise to nitrogen peroxide, it will react with sulphuric acid in accordance with the equation $2\text{NO}_2 + \text{H}_2\text{SO}_4 = \text{HNO}_3 + \text{HNOSO}_4$, and on electrolysis of the nitrososulphuric acid, the following reaction may take place: $\text{HNOSO}_4 + 2\text{H}_2\text{O} = \text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{H}_2 + 2 \text{ farads}$. In practice, however, the process is only efficient at first, since nitric acid or nitrososulphuric acid diffuses through the diaphragm and is reduced to nitric oxide with some free nitrogen. The chemical reactions involved in the conversion of nitric oxide to nitric acid in the arc and ammonia oxidation processes are:



Of these reactions, the first is the controlling one, and for this reason as much space as practicable should be allowed for the reaction in the plant. This reaction begins to proceed from left to right as soon as the gases have cooled below 600° , but is not complete even in the presence of a large excess of oxygen until the temperature reaches 200° . Since the reaction has a negative temperature coefficient, it is necessary to cool the gases as much as possible before entering the absorption system. [See also *J. Soc. Chem. Ind.*, June.]

C. A. M.

Amount of Phosphoric Acid in the Sea-water off Plymouth Sound. DONALD J. MATTHEWS (*Reprint: J. Marine Biol. Assoc. United Kingdom*, 1917, 11, 251—257. Compare A., 1916, ii, 635).

—The amount of phosphoric acid in sea-water off Plymouth reached a maximum (0.06 mg. of P_2O_5 per litre) in December, 1915; it then decreased irregularly to a minimum (less than 0.01 mg. per litre) in April—May, 1916, and again attained the same maximum as before in January, 1917. This seasonal variation is probably due to the removal of phosphates from solution by algae, diatoms, etc.

W. P. S.

The Fundamental Polyhedron of the Diamond Lattice.

ELLIOT Q. ADAMS (*J. Washington Acad. Sci.*, 1918, 8, 240).—The author has found that the convex polyhedron with a symmetry corresponding with the point-system of the diamond space-lattice is the dodecatetrahedron $k(111), (110)$. The arrangement of this in space constitutes a kind of twinning, which explains the fact that diamond is crystallographically holohedral, but the unit polyhedra are hemihedral.

A. B. S.

Oxidisable Constituents of Coal. I. J. I. GRAHAM and J.

HILL (*Trans. N. Eng. Inst. Min. Eng.*, 1918, 68, 37—54).—Coal from the Barnsley soft seam was extracted with pyridine at 40° and 60 mm. pressure in an atmosphere of nitrogen. This was intended to prevent or minimise the absorption of oxygen and pyridine by the coal, which probably occurred in previous experiments on the extraction of coal with solvents. Ten to fifteen % of extract was obtained. The capacity for absorbing oxygen was determined for the extract, the residue, and the original coal by Winmill's method at 30° and 90°, both in air and an atmosphere of 90% oxygen. The absorption by the extract was negligibly small, whilst the avidity of the residue for oxygen was almost equal to that of the original coal. The humic and not the resinic constituent of this coal is the one responsible for tendency to spontaneous combustion. The extract, unlike those described by Wheeler (T., 1913, 103, 1713), was inert towards a photographic plate, whilst the residue showed a great activity, not, however, due to the oxidation. [See, further, *J. Soc. Chem. Ind.*, 262a.]

H. J. H.

Carbonation. II. Carbonation of Distilled Water.

H. E. PATTEN and G. H. MAINS (*J. Ind. Eng. Chem.*, 1918, 10, 279—288).—The rate of evolution of carbon dioxide from distilled water impregnated with carbon dioxide under pressure at 0° was measured by opening the bottle momentarily and noting the time required until the initial pressure was again shown on the pressure gauge. In this way, a series of simultaneous measurements of pressures and times was obtained, and from these data "pressure recovery" curves were constructed, in which the time in minutes represented the abscissæ and the pressure in lb. per square inch

in excess of atmospheric pressure formed the ordinates. With the exception of the first curve corresponding with the first opening, in which an excessive quantity of gas was withdrawn, the curves showed a striking regularity, and were, in general, of a logarithmic type. The anticipated sudden rise of curve and sharp decrease of pressure were not observed. The results indicated that at a high pressure of carbon dioxide there is a close agreement with Henry's law. [See also *J. Soc. Chem. Ind.*, June.] C. A. M.

Theoretical and Experimental Investigations on Metallic Alloys. N. PARRAVANO (*Ann. Chim. Applicata*, 1918, 9, 1-86).

—The author brings together the results of investigations on binary, ternary, and quaternary alloys made by himself and his collaborators and by De Cesaris, and already published in a series of thirty-seven papers during the years 1910-1917.

T. H. P.

The Stability of Dakin's Sodium Hypochlorite Solution.

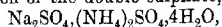
FRITZ WISCHO and FRANZ FREIBERGER (*Münch. med. Woch.*, 1917, 64, 1528-1529; from *Chem. Zentr.*, 1918, i, 228).—Concentrated Dakin solutions deteriorate to the extent of about 40% of the sodium hypochlorite in a month; they are comparatively stable when the amount of hypochlorite is reduced to 12.5%, but dilute solutions will keep better still, the decomposition being only about 10% in two months.

J. C. W.

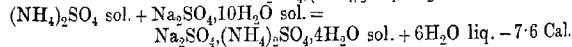
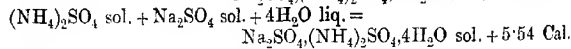
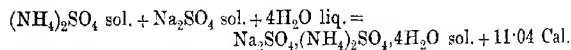
The Double Sulphate of Sodium and Ammonium.

C. MATIGNON and F. MEYER (*Compt. rend.*, 1918, 166, 686-688).

—The heat of solution of the double sulphate,



at about 15° is -13.00 Cal., from which the following heats of formation of the double salt may be deduced:



The double salt is stable in the presence of its saturated solution between the temperature limits of 20° and 42°, and thus the salt may be prepared by evaporating a solution containing equimolecular proportions of the two generating salts between these temperatures.

W. G.

Crystals of Barium Disilicate in Optical Glass. N. L.

BOWEN (*J. Washington Acad. Sci.*, 1918, 8, 265-268).—Colourless, six-sided crystal plates with opaque white rims, which form in optical glass rich in barium have been identified with crystals of BaSi_2O_5 prepared synthetically. The white outlines are due to minute

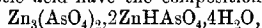
crystals which lie along the edges of the larger ones. A small amount of alkali disilicate appears to be contained in solid solution in the crystals in the glass. The plates are orthorhombic crystals with terminal angles 100° , lateral angles 130° , good cleavage parallel to elongation, negative elongation and optical character with $2V=70^\circ$, refractive indices, $\gamma=1.617$, $\alpha=1.598$ in synthetic crystals, slightly lower in crystals in glass, isomorphous with $K_2Si_2O_5$.
A. B. S.

The Ternary System, $MgO-Al_2O_3-SiO_2$. G. A. RANKIN and H. E. MERWIN (*Amer. J. Sci.*, 1918, [iv], **45**, 301–325).—The ternary system, magnesia-alumina-silica, has been investigated thermally to determine the melting temperatures of the various phases and microscopically to identify the various crystalline substances produced. The various boundary curves of the phases have been determined and the quintuple points fixed. It is shown that the following crystalline substances are stable in contact with the liquid phase: periclase (MgO), corundum (Al_2O_3), tridymite (SiO_2), forsterite ($2MgO, SiO_2$), clinoenstatite (MgO, SiO_2), spinel (MgO, Al_2O_3), sillimanite (Al_2O_3, SiO_2), and a ternary silicate, $2MgO, 2Al_2O_3, 5SiO_2$, which may be regarded as an end member in the cordierite series. The last compound is unstable at its melting point, and is considerably affected by solid solution. It has been observed in two forms; the α -form (unstable) crystallises from glass at temperatures below 950° , and is transformed at a somewhat higher temperature into the stable (α) form. The properties of both forms, but more especially those of the α -form, are very like those of the mineral cordierite. Seven quintuple points have been established, two of which are eutectics. The first lies at $1345^\circ \pm 5^\circ$, and is for MgO, SiO_2 , SiO_2 and the ternary compound; the second lies at $1425^\circ \pm 5^\circ$, and is for $SiO_2-Al_2O_3, SiO_2$ and the ternary compound. The third point lies at $1460^\circ \pm 5^\circ$, and is for $Al_2O_3, SiO_2-MgO, Al_2O_3$ and the ternary compound; the fourth point lies at $1370^\circ \pm 5^\circ$, and is for spinel— $2MgO, SiO_2$ and the ternary compound. Point five lies at $1560^\circ \pm 5^\circ$, and is for $2MgO, SiO_2-MgO, SiO_2$ and the ternary compound. The sixth quintuple point is the eutectic point for $2MgO, SiO_2-MgO$ and spinel. It has a melting point $1700^\circ \pm 25^\circ$. The last point lies at $1575^\circ \pm 5^\circ$, and is for Al_2O_3 , spinel, and Al_2O_3, SiO_2 . The whole of the experiments were carried out either in a platinum resistance furnace for temperatures below 1600° or in an iridium furnace for higher temperatures. Diagrams and solid models of the system are given to illustrate the equilibria.
J. F. S.

Influence of Cadmium on the Properties of Alloys of Copper and Zinc. LÉON GUILLET (*Compt. rend.*, 1918, **166**, 735–737).—A study of the effect of introducing from 0–4% of cadmium into brasses containing 60% or 70% copper on the mechanical properties of the alloy. Values are tabulated for the

traction, shock, and hardness constants of the alloys, and notes on their micro-structure are given. [See, further, *J. Soc. Chem. Ind.*, June.] W. G.

Colloidal Arsenates. G. KLEMP and J. VON GYULAY (*Kolloid Zeitsch.*, 1918, **22**, 57—68. Compare A., 1915, ii, 256).—If solutions of potassium dihydrogen arsenate and zinc sulphate of appropriate concentration are brought together, there is no precipitation, but a jelly containing zinc hydrogen arsenate is formed. The same result is obtained if the zinc sulphate solution is mixed with solutions of disodium hydrogen arsenate or trisodium arsenate which have been previously neutralised by the addition of hydrochloric or acetic acid. When the jellies are kept for two or three months, crystals begin to separate. The crystals which separate from the jellies prepared from trisodium arsenate neutralised by acetic acid have the composition



whilst those separating from the jellies prepared from potassium dihydrogen arsenate or from trisodium arsenate neutralised by hydrochloric acid consist of zinc hydrogen arsenate, $\text{ZnHAsO}_4 \cdot \text{H}_2\text{O}$. H. M. D.

Sub-bromide and Sub-chloride of Lead. HENRY GEORGE DENHAM (T., 1918, **113**, 249—256).—The method previously described for the preparation of lead sub-iodide (T., 1917, **111**, 29), has been extended to the corresponding bromine and chlorine compounds, the sub-bromide being obtained by the action of ethyl bromide vapour on lead sub-oxide at 261°, and the sub-chloride by the action of ethyl chloride on the sub-oxide at 311°. The two sub-compounds are grey in colour, fairly stable in the air, but are readily oxidised by bromine water or by permanganate solution. They are readily decomposed by acids with the formation of the normal salts and the metal.

The sub-salts are sparingly soluble in water. On the assumption that the salts are completely ionised and that the ions have the same mobility as those of the normal salts, the electrical conductivities of the saturated solutions give 2.2 milli-equivalents per litre for the solubility of the sub-chloride and 0.4 milli-equivalent for that of the sub-bromide. H. M. D.

The Rare Earths. V. Holmium and Dysprosium. H. C. KREMERS and C. W. BALKE (*J. Amer. Chem. Soc.*, 1918, **40**, 593—598. Compare A., 1917, ii, 259, and following abstract).—The concentration of dysprosium and holmium in a mixture of the yttrium earths, and the separation of holmium from yttrium have been studied. It is found that the fractionation of the bromates of the yttrium earths effects a rapid and efficient concentration of dysprosium and holmium. Starting with 12 kilos. of rare earth oxalates from gadolinite, which were converted into bromates, three parallel series of fifty recrystallisations were carried out. The series showed a concentration of

samarium, neodymium, and praseodymium toward the insoluble end, dysprosium and holmium in the central portion, and yttrium, thulium, and erbium toward the soluble end. At this point, the material rich in dysprosium and holmium was removed from the three series, combined, and made into three new series, *A*, *B*, and *C*. Series *A* consisted of the more soluble fractions, and contained dysprosium, holmium, erbium, and yttrium. Series *B* contained the fractions richest in holmium and dysprosium, with small amounts of neodymium, praseodymium, erbium, and yttrium. Series *C* was composed of the less soluble bromates, and contained holmium, dysprosium, terbium, neodymium, praseodymium, and traces of erbium and yttrium. The three series were fractionated in parallel. The concentration of the earths in the different series was controlled mainly by the colour of the solutions. As the holmium and dysprosium became concentrated toward the less soluble end of series *A*, these fractions were added to series *B*, placing them where the fractions showed a similar colour. From series *C*, the more soluble dysprosium and holmium were removed and added to series *B* in the same way. In the same manner, yttrium and erbium which collected in the soluble end of series *B* were added to series *A*, and the neodymium and praseodymium from the less soluble end of *B* were placed in *C*. The three series were recrystallised thirty times, which caused most of the dysprosium and holmium to collect in series *B*; was eventually given a further sixty recrystallisations, which caused the holmium and dysprosium to concentrate very rapidly. A difficulty was experienced due to the repeated separation of cerium basic bromate as a brown sludge. It is therefore recommended that the cerium be removed by the sodium sulphate method before the fractionation commences. The separation of holmium from yttrium was also studied (i) by fractional precipitation with lactic acid, (ii) by fractional precipitation with ammonium carbonate, and (iii) by fusion of the nitrates. The first two methods were entirely unsuccessful. The fusion of a mixture of samarium, yttrium, and holmium nitrates gave a rapid concentration of the holmium. A mixture which had an equivalent of 98.6 at the start gave after thirty-one fusions four end fractions with equivalents 154.2—155.3. Attempts to separate holmium and yttrium by this method failed, and it was only after the addition of samarium that the separation became possible. J. F. S.

The Rare Earths. VI. Purification and Atomic Weight of Dysprosium. H. C. KREMERS, B. S. HOPKINS, and E. W. ENGLE (*J. Amer. Chem. Soc.*, 1918, **40**, 598—611. Compare *A.*, 1917, ii, 259, and preceding abstract).—A short history of the knowledge of the element dysprosium is given in the paper. A quantity of dysprosium material of a high state of purity was further fractionated as ethyl sulphates and as bromates. It is shown that the ethyl sulphates are more efficient for the separation of dysprosium from neodymium, praseo-

dymium, and terbium, and that neither of the methods is efficient for the separation of holmium from dysprosium. The atomic weight of dysprosium has been determined from the ratios (i) dysprosium sulphate to dysprosium oxide, (ii) dysprosium oxide to dysprosium chloride, and (iii) dysprosium chloride to silver. It is shown that the octahydrate of dysprosium sulphate is not constant in composition when dried over sulphuric acid, consequently the ratio $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O} : \text{Dy}_2\text{O}_3$ does not give trustworthy values for the atomic weight. The value $\text{Dy} = 163.83$ was obtained as the mean of nine experiments from the ratio $\text{DyCl}_3 : \text{Dy}_2\text{O}_3$, but since, on further investigation, it was shown that the oxide prepared for these experiments from the oxalate was not constant in composition, this value is rejected. By no method tried could an oxide be obtained which yielded concordant results from this ratio. Eight experiments were made to determine the ratio $\text{DyCl}_3 : 3\text{Ag}$, and the value 162.52 obtained. This is put forward as the most likely value, and is considerably lower than the result obtained (164.228) previously (*loc. cit.*). J. F. S.

Determination of the Velocities of Cooling necessary to realise the Tempering of Carbon Steels. P. CHEVENARD (*Compt. rend.*, 1918, **166**, 682—685).—A continuation of previous work (compare A., 1917, ii, 414). Using the method previously described (*loc. cit.*), and working with steels containing from 0.2—0.8% carbon, the author has determined, for different temperatures of heating, in the diagram plotting carbon content against velocity of cooling, the curves which mark the limit of appearance of martensite. The results indicate that, from the point of view of the effectiveness of tempering, an insufficient velocity of cooling can, to a certain extent, be compensated by an elevation of the temperature of heating. This compensation is less adequate as the carbon content of the steel diminishes. [See, further, *J. Soc. Chem. Ind.*, June.] W. G.

The Reduction of Osmium Tetroxide by Hydrogen Chloride. JAROSLAV MILBAUER (*J. pr. Chem.*, 1917, [ii], 96, 187—189).—During experiments the results of which indicated that the chlorides of most metals are without appreciable influence on the rate of oxidation of aqueous hydrogen chloride by free oxygen or air, it has been found that, contrary to the general belief (compare Dammer, "Handbuch," III, p. 919), osmium tetroxide is reduced by concentrated hydrochloric acid with production of chlorine, the chemical change being representable by the equation $2\text{OsO}_4 + 12\text{HCl} = 2\text{OsO}_3 + 6\text{Cl}_2 + 6\text{H}_2\text{O}$. D. F. T.

Mineralogical Chemistry.

The Auriferous Minerals of the Côte d'Ivoire. F. ROUX (*Compt. rend.*, 1918, 166, 645—646).—A sample of the metallic portion of a quartz, without visible gold, from Kokumbo gave on analysis: Au=8.63%, Bi=48.36%, Cu=1.82%, Te=37.52%, Ag=trace, S=3.65%. Two metallic samples from the mineral at Poréssou were each found to contain tellurium and bismuth.

W. G.

Analytical Chemistry.

Accurate Method for taking "Aliquots" in Volumetric Analysis. HERBERT E. EASTLACK (*J. Amer. Chem. Soc.*, 1918, 40, 620—622).—The author describes a method of taking aliquot parts of solutions for analysis, based on that of Miller (this vol., ii, 80), which is claimed to be simpler, more rapid, and more accurate than Miller's method. The newer method differs from the earlier one mainly in titrating the residue after the titrations have been made, instead of evaporating to dryness and weighing it.

J. F. S.

Detection and Estimation of Bromine by Magenta-Sulphuric Acid Reagent. G. DENIGÈS and L. CHELLE (*Ann. Chim. anal.*, 1918, 23, 81—83).—The influence of nitrous acid on the detection of bromine by the magenta-sulphuric acid method described previously (A., 1913, ii, 72) may be prevented by carrying out the test at a temperature not exceeding 16°. Five c.c. of the bromide solution (containing not more than 1 gram of bromine per litre) are treated with 4 drops of concentrated hydrochloric acid, 4 drops of 10% potassium chromate solution, and 1 c.c. of concentrated sulphuric acid; the mixture is cooled at once to 15°, and 1 c.c. of the magenta reagent and 1 c.c. of chloroform are added; the chloroform is coloured red when the mixture is shaken, the intensity of the coloration depending on the quantity of bromine present.

W. P. S.

New General Method for Determining Iodine in Inorganic and Organic Compounds. N. TARUGI (*Gazzetta*, 1918, 48, i, 1—16).—This method is based on the reaction $6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{ICl}_3 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{I}_2 + 6\text{HCl}$. The iodine formed is extracted by means of chloroform and titrated with thiosulphate, whilst the chlorine is determined by titrating with permanganate

the residual acid solution from the extraction, this containing the ferric sulphate and the excess of the ferrous sulphate. In this way, the proportions of iodine and chlorine, and thus those of iodine trichloride and monochloride in a solution of iodine trichloride, are obtained.

By simple methods, the iodine in an inorganic or organic compound may be converted into iodine trichloride and then estimated as above. [See, further, *J. Soc. Chem. Ind.*, 285A.] T. H. P.

Oxidation of Sulphides with Potassium Iodate.

REGINALD S. DEAN (*J. Amer. Chem. Soc.*, 1918, **40**, 619—620).—In a previous paper (A., 1915, ii, 480), it was shown that in the estimation of sulphides by oxidation with potassium iodate in the presence of hydrochloric acid, the amount of sulphur oxidised to sulphuric acid depended on the concentration of the acid, and that with an amount of iodate equivalent to the sulphide, the maximum amount of oxidation is represented by the equation $3\text{MS} + 3\text{KIO}_3 + 12\text{HCl} = 3\text{MCl}_2 + 2\text{S} + \text{H}_2\text{SO}_4 + 3\text{KCl} + 3\text{HCl} + 5\text{H}_2\text{O}$. It is now shown that with an excess of iodate and hydrochloric acid of any strength sufficient to prevent the hydrolysis of the iodine chloride formed, the whole of the sulphur is quantitatively oxidised to sulphuric acid according to the equation $\text{H}_2\text{S} + 2\text{KIO}_3 + 4\text{HCl} = 2\text{HCl} + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{KCl}$. The estimation is carried out as follows. A solution of hydrogen sulphide is treated with the requisite excess of potassium iodate solution and hydrochloric acid (6—3*N*), and the excess of iodate estimated by means of a standard iodine solution. The method has also been applied to the estimation of lead sulphide; the freshly precipitated lead sulphide is introduced into the iodate solution, hydrochloric acid added, and the titration completed as before. The results in both cases agree within 0.1% of the theoretical value. J. F. S.

The Estimation of Thio-esters in Urine. LUCIEN CORDIER (*J. Pharm. Chim.*, 1917, [vii], **16**, 360—363).—The author considers that Gauvin's method (A., 1914, ii, 142) of hydrolysis of the thio-esters by boiling the urine with one-fifth its volume of hydrochloric acid for fifteen minutes gives satisfactory results in the estimation of these constituents in urine. W. G.

Two Methods of Destruction of Organic Substances in Urine. LUCIEN CORDIER (*J. Pharm. Chim.*, 1917, [vii], **16**, 363—367).—In the first method, 20 c.c. of urine are evaporated to dryness with 4 grams of a mixture of equal parts of potassium nitrate, anhydrous potassium carbonate, and anhydrous sodium carbonate. The dry residue is intimately mixed with a further 8 grams of the fusion mixture and fused until all the carbon is oxidised. The second method is a modification of that of Gautier and Clausmann for animal tissues (compare A., 1917, ii, 421). Twenty c.c. of urine are evaporated to dryness with 2 grams of magnesium nitrate, and the dry residue is strongly heated until

all the carbon is burnt off. The residue from either fusion may be used for the estimation of total sulphur in urine. W. G.

Detection of Carbon Dioxide in the Analysis of Carbonates or Oxalates. O. F. STAFFORD (*J. Amer. Chem. Soc.*, 1918, **40**, 622).—In order to detect the presence of carbon dioxide in the gaseous products of the action of acids on minerals, the author inserts a glass tube into the mouth of the test-tube; this tube is drawn out to a capillary fine enough to cause a drop of the reagent (baryta water) to remain in it, and not too fine to prevent bubbles of the gas being drawn upward through the liquid. To make the test, the gas from the test-tube is drawn through the baryta water by aspirating at the top of the inserted tube. The method may be made roughly quantitative for small traces of carbonates or oxalates. Two such capillaries are used; the material to be examined is placed in one, and the second tube, containing a drop of baryta water, inserted into the mouth of the first and sealed to it by means of "Khotinsky" cement. Then by aspirating a drop of 30% sulphuric acid is drawn on to the material, and the gas generated drawn through the baryta water. In the case of oxalates, 30% sulphuric acid mixed with potassium permanganate is used. The turbidity produced in the baryta water is compared with turbidities produced similarly from known amounts of carbonates or oxalates. J. F. S.

Water Analysis in the Field. GEORGE W. HEISE and A. S. BEHRMAN (*Philippine J. Sci.*, 1918, **13**, [A], 1—17).—The methods are based on those of Leighton [U.S. Geol. Survey, Water Supply Paper (1905) No. 151], and bacteriological examination is also made. Titrations are effected with reagents in pellet form. [See, further, *J. Soc. Chem. Ind.*, June.] H. J. H.

Detection of Potassium by the Use of Light Filters. ALOIS HERZOG (*Chem. Zeit.*, 1918, **42**, 145).—The light filter recommended is prepared by coating a glass plate with a gelatin solution containing a mixture of the two dyes patent blue and tartrazin in such proportion that each sq. metre of glass shall have on it 3.9 grams of the former and 2.5 grams of the latter dye. Viewed through this screen, the potassium flame appears bright red surrounded by a yellowish-green fringe. Rubidium is the only other element which gives a coloration similar to that shown by potassium. Green and violet dyes may be used for the purpose, but preference is given to the mixture mentioned. W. P. S.

Iodide Titration of Silver Nitrate with Palladous Nitrate as Indicator. LOUIS SCHNEIDER (*J. Amer. Chem. Soc.*, 1918, **40**, 583—593).—The Volhard method for the volumetric estimation of silver is interfered with by the presence of certain metals and loses its sensitiveness for very dilute solutions. The

author describes a method whereby silver solutions may be titrated with iodide in the presence of such metals and in very dilute solution by use of a solution of palladous nitrate as indicator. The indicator is prepared by dissolving 0.06% of palladous nitrate in 16% nitric acid; it is found advisable to use a protective colloid along with the indicator to prevent the occlusion of potassium iodide or silver nitrate. For this purpose, a 5% solution of gum arabic is found most advantageous. The indicator is converted by the first excess of iodide into palladous iodide, which gives a red colour to the solution; this action is sensitive to 1 part in 500,000. This method is further to be recommended on account of the accuracy and easy reproducibility with both $N/10$ - and $N/1000$ -solutions. The author discusses at some length the possible errors of the method, and gives full details of the procedure to be adopted for $N/10$ - and $N/1000$ -solutions. J. F. S.

Field Methods for the Determination of the Total Hardness of Water. A. S. BEHRMAN (*Philippine J. Sci.*, 1918, 13, [A], 21—27).—Blacher's method of titration with potassium palmitate has been adapted to field conditions. The water is titrated with standard pellets of the reagent. [See, further, *J. Soc. Chem. Ind.*, June.] H. J. H.

Analysis of Glass. L. RONNET (*Ann. Falsif.*, 1918, 11, 26—31).—A scheme is given for the analysis of glass containing silica, iron, aluminium, manganese, calcium, magnesium, potassium, and sodium. The usual methods of separating and estimating these constituents are employed. [See, further, *J. Soc. Chem. Ind.*, 1918, 266A.] W. P. S.

Estimation of the Reducing Power of Urine, both free from and containing Dextrose, by means of an Alkaline Glycerol-Copper Solution. H. RUOSS (*Zeitsch. physiol. Chem.*, 1918, 101, 131—164).—The method previously described (A., 1917, ii, 549) is modified by employing a glycerol-copper solution and by using always the same volume of urine with varying quantities of copper solution instead of maintaining a constant volume of the latter and varying the former. The glycerol-copper solution is prepared by dissolving 3.464 grams of copper sulphate in 10 c.c. of hot water, cooling, and adding 15 c.c. of glycerol and 22 c.c. of sodium hydroxide solution (D 1.357). The mixture is again cooled, 5 c.c. of a 30% potassium thiocyanate solution added, and then the volume brought to 100 c.c. by the addition of 25% sodium chloride solution. For an estimation, 5 c.c. of urine are treated with from 0.1 to 1 c.c. of the new reagent, and, after boiling, the end-point determined in the manner previously described (*loc. cit.*). The amount of copper solution is varied until it is exactly reduced by the dextrose or other reducing substances present in the urine.

Attention is directed to the fact that the reducing power of urine free from sugar is proportional to $D-1$, where D is the

specific gravity of the urine, and that the urine may be freed from substances containing nitrogen by treatment with an excess of the Patein-Schöndorff mercuric nitrate reagent (A., 1908, ii, 311), the excess of mercury being subsequently removed by precipitation with alkali followed by zinc dust.

H. W. B.

Copper-Phosphate Mixtures as Sugar Reagents. A Qualitative Test and a Quantitative Titration Method for Dextrose in Urine. OTTO FOLIN and W. S. McELROY (*J. Biol. Chem.*, 1918, **33**, 513—519).—The qualitative reagent is prepared by dissolving 100 grams of sodium pyrophosphate (U.S.P.), 30 grams of crystallised disodium hydrogen phosphate, and 50 grams of anhydrous sodium carbonate in about a litre of water, and adding 13 grams of copper sulphate previously dissolved in about 200 c.c. of water. The solution appears to keep indefinitely and is cheaply prepared. To test for reducing sugars, 5 c.c. of the reagent are placed in a test-tube, five to eight drops (not more than 0.5 c.c.) of the urine added, and the mixture boiled for one minute, or heated in boiling water for three to five minutes. Minute traces of sugar are indicated by various grades of turbidity, larger amounts by unmistakable precipitates of cuprous oxide. A slight turbidity occurring after cooling may be due only to the reducing action of normal urine.

For quantitative estimation, the only solution required is an acidified copper sulphate solution containing 60 grams of crystallised copper sulphate and 4 c.c. of concentrated sulphuric acid per litre. Five c.c. of this solution correspond with 25 mg. of dextrose or levulose, 45 mg. of anhydrous maltose, or 40.4 mg. of anhydrous lactose. The other necessary reagent is a dry mixture containing 100 grams of crystallised disodium hydrogen phosphate, 60 grams of dry sodium carbonate, and 30 grams of sodium or potassium thiocyanate. The authors recommend the titrations to be made in test-tubes, using undiluted urine. This simplification is made possible by attaching to the tip of an ordinary 25 c.c. glass-stoppered burette another tip consisting of a glass tube drawn out at one end to an almost capillary bore, and delivering between forty-five and fifty-five drops of urine per c.c. If the burettes carrying accessory tips are filled by suction, the necessity of rinsing the burette with the sugar solution to be titrated is avoided, which can be proved by filling the burette with water after it has just been emptied from a urine containing 5% of sugar. On testing the water in the lower part of the burette, it is found to be quite free from sugar. To carry out an estimation, 5 c.c. of the copper reagent and 4 to 5 grams of the dry salt mixture are heated in a test-tube until a clear solution is obtained (a pebble is added to prevent bumping). Twenty-five drops of urine are run in from the burette, and the mixture gently boiled for two minutes. If the solution is still blue, more urine is run in, boiling for one minute after each addition, until the solution is colourless. From the total number of drops, the volume of urine added can be computed,

and hence the percentage of dextrose in the urine. The results of the titration should be confirmed by a repetition, in which the first addition of urine should be only two or three drops less than the full amount of urine required. The total period of boiling must not be less than four or more than seven minutes.

The presence of albumin in the urine does not obscure the end-point of the titration. The use of the test-tube instead of a flask or beaker greatly retards the reoxidation of the cuprous oxide and materially aids the rapid performance of the test. If desired, a 5 c.c. burette graduated in 0.02 c.c. divisions may be used instead of the ordinary burette with capillary tip described above.

H. W. B.

Estimation of Lactose in Milk. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1918, **33**, 521—524).—The authors describe two methods, based on titration and colorimetry respectively, the former being considered to give the more nearly accurate results. In the titration method, the reagents and apparatus described for the estimation of dextrose in urine (preceding abstract) are employed, and neither the protein nor the fat is previously removed from the milk. The milk is simply diluted with water (1:4) and added directly to the copper-phosphate solution, boiling being continued rather longer than in the estimation of dextrose.

For the colorimetric estimation, a modification of Dehn and Hartman's method (A., 1914, ii, 223) is described which is based on the colour developed when an alkaline solution of lactose in saturated picric acid is heated for a fixed time at 100°. [See, further, *J. Soc. Chem. Ind.*, 278A.]

H. W. B.

Estimation of Dicyanodiamide in Old Calcium Cyanamide. H. KAPPEN (*Zeitsch. angew. Chem.*, 1918, **31**, 31—32).—A sample of very old calcium cyanamide was found to be free from cyanamide nitrogen; the dicyanodiamide nitrogen was estimated by Caro's and by Hager's methods. The results obtained by these two methods did not agree (compare Hager and Kern, A., 1916, ii, 687), and the author suggests that the difference may be due, in part, to the presence of urea in the sample. This is confirmed by the results of analyses of mixtures of urea and dicyanodiamide; urea has less effect on the results obtained by Caro's method than it has on those found by Hager's method.

W. P. S.

The Spectroscopic-quantitative Estimation of Urochromogen. TRAUGOTT BAUMGÄRTEL (*Biochem. Zeitsch.*, 1918, **85**, 162—170).—The author gives a modification of the method of Weiss for the estimation of urochromogen by oxidation with potassium permanganate, in which the colorimetric method adopted by Weiss is replaced by the detection of excess of permanganate spectroscopically. The method has been applied to the determination of the urochromogen output in the urine in certain pathological cases.

S. B. S.

